

Dynamical Correlations for Statistical Copolymers from High-Throughput Broad-Band Dielectric Spectroscopy

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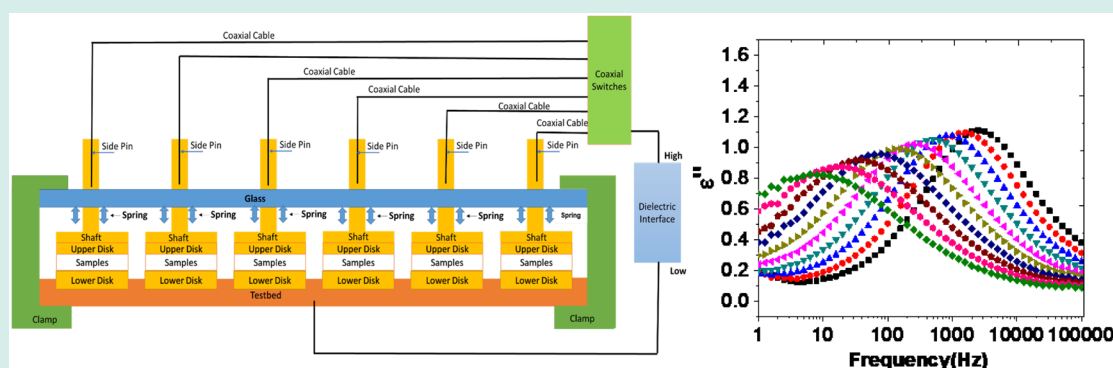
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Supporting Information



ABSTRACT: Broad-band dielectric spectroscopy (BDS) provides a powerful method of characterizing relaxation dynamics in diverse materials. Here we describe and employ a novel instrument for high-throughput broad-band dielectric spectroscopy (HTBDS) that accelerates this capability, enabling simultaneous measurements of 48 samples. This capability is based around a coaxial switching system for rapid scanning between multiple samples on the same sample stage, coordinated with shared environmental control. We validate the instrument by measuring dielectric response in three polymers, distributed across 48 sample sites, and comparing results to measurements via a standard BDS instrument. Results are found to be reproducible and are in agreement with relaxation times from traditional BDS. We then employ HTBDS to establish mixing rules for glass transition temperatures, kinetic fragility indices, and segmental stretching exponents in a series of acrylate copolymers, a matter of considerable technological interest in a variety of technological applications. Results are consistent with the empirical Fox rule for the glass transition temperature T_g averaging in polymer blends, while they reveal a linear mixing rule for kinetic fragility indices. Finally, we test several proposed correlations between these distinct dynamical properties. These results demonstrate that HTBDS enables measurements of polymer relaxation at a throughput approximately 10 times higher than that of standard BDS approaches, opening the door to high-throughput materials design of dynamic response across a broad range of frequencies.

KEYWORDS: broadband dielectric spectroscopy, glass transition, copolymers

INTRODUCTION

Broad-band alternating current (ac) dielectric spectroscopy (BDS) employs interactions between materials and an imposed ac electrical field (with frequencies ranging from 10^{-6} to 10^{12} Hz) to probe material properties.¹ The resulting dielectric relaxation spectra are sensitive to material properties of relevance in many systems, including liquid crystals,^{2–5} ionic liquids,^{6–9} semiconducting materials,^{10–12} glass-forming liquids,^{13–19} polymeric materials,^{20–24} and nanoconfined systems,^{25,26} among others. In the 10^9 – 10^{-2} Hz frequency range, the dielectric response can report on both structural relaxation and ionic conductivity, providing access to multiple

technologically relevant properties over a large range of rates and temperatures. This metrology is therefore of considerable interest both in probing fundamental material physics and in aiding materials design.

Given its versatility, BDS would seem to provide an ideal metrology for materials screening, combinatorial study, and library building. The primary factor currently gating this type of use is the duration of a BDS experiment: a typical BDS experiment

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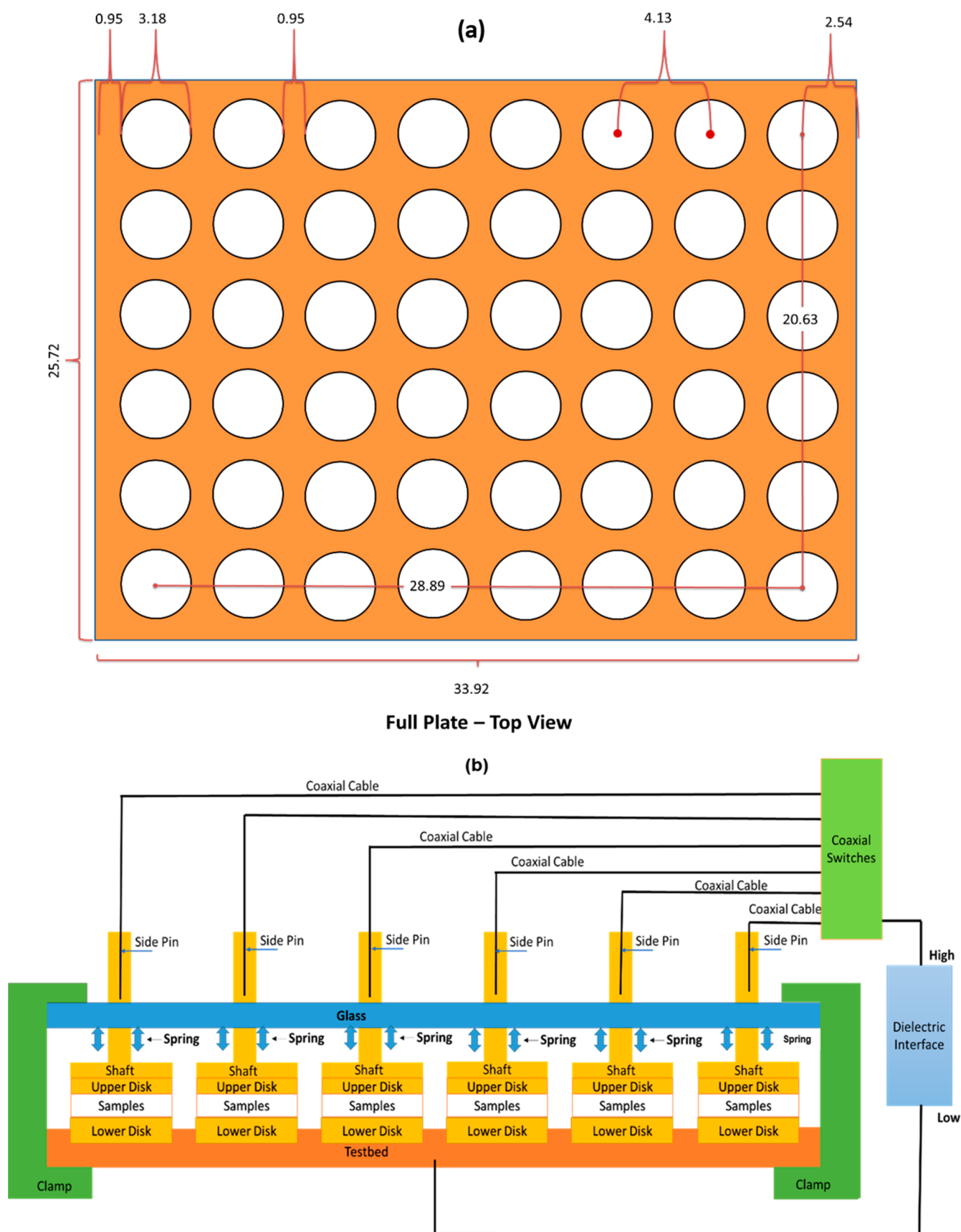


Figure 1. Schematics of the HTDS assembly: (a) top view of the testbed; (b) side view of the entire assembly. The schematic is not to scale. Dimensions in the upper figure are given in cm.

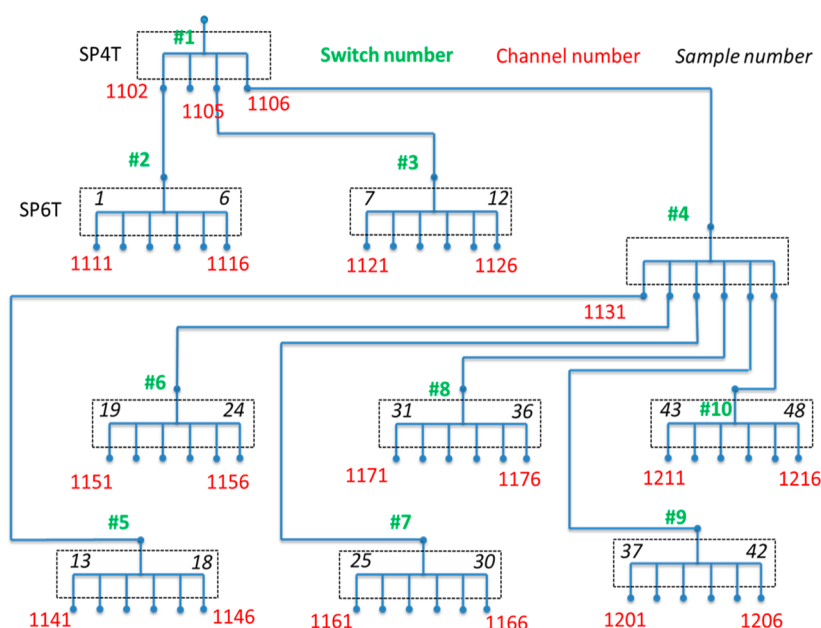


Figure 2. Schematic of switch connections.

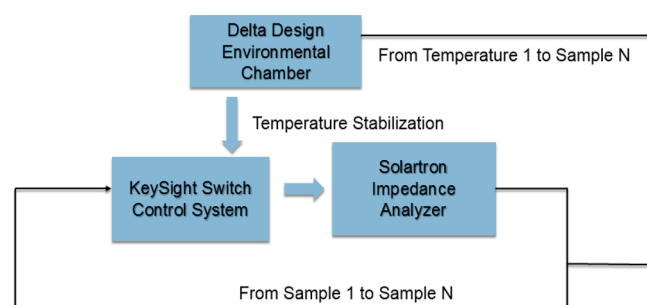


Figure 3. Operation protocol of the LabVIEW control.

probing dielectric response of a single material over a large frequency and temperature range can require 12 h or more. In order to enable higher-throughput use of BDS, here we describe its extension to the parallel measurement of multiple samples. This technique, high-throughput broad-band dielectric spectroscopy (HTBDS), enables parallel measurement of dielectric response in 48 distinct material samples, with applications for the accelerated discovery of novel materials and elucidation of materials physics.

A temperature-sweep/frequency-sweep BDS experiment of the type described above consists of iterative measurement of dielectric response over a range of frequencies at a series of predefined temperature set points. Except for measurements at very low frequency, the rate-limiting step in this process is generally thermal equilibration. For example, in commercially available cryostat-based single sample stages, proper thermal equilibration, i.e., temperature variations of less than or equal to ± 0.1 K,²⁷ after a 5 K temperature step requires approximately 40 min. Dielectric response over a frequency range of 10^6 – 10^{-1} Hz can then be assayed at that temperature in 4–8 min before moving on to the next temperature, depending on the frequency resolution. The majority of time consumed in a typical experiment is thus spent on thermal equilibration rather than on measurement itself.

The HTBDS implementation described here improves the throughput of this metrology by parallelizing the thermal equilibration step of the measurement across numerous samples. HTBDS incorporates 48 sample sites into a single sample stage within a single environmental control chamber. This strategy enables simultaneous thermal equilibration of all 48 samples in

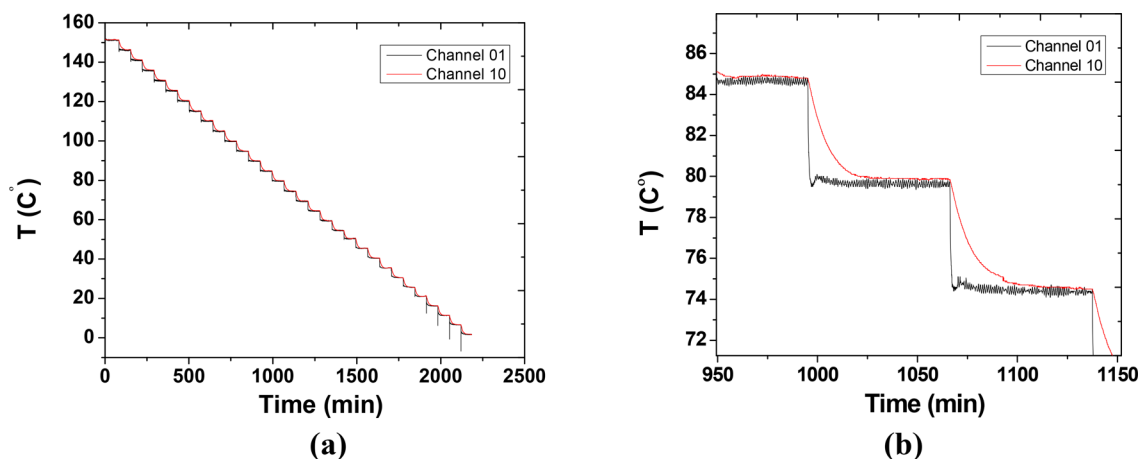
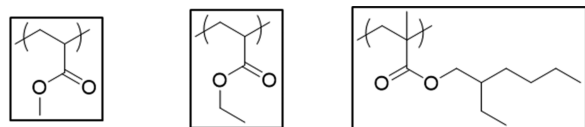


Figure 4. (a) Overall range of the temperature vs time curve. (b) Enlarged version of the temperature vs time curve.



Poly(methyl acrylate) Poly(ethyl acrylate) Poly(2-ethylhexyl methacrylate)

Figure 5. Molecular structures of the tested polymers.

Table 1. Input Parameters for the HTDS LabVIEW Program

initial temp	final temp	cooling step	equilibration time
326.15 K	262.15 K	4 K	40 min

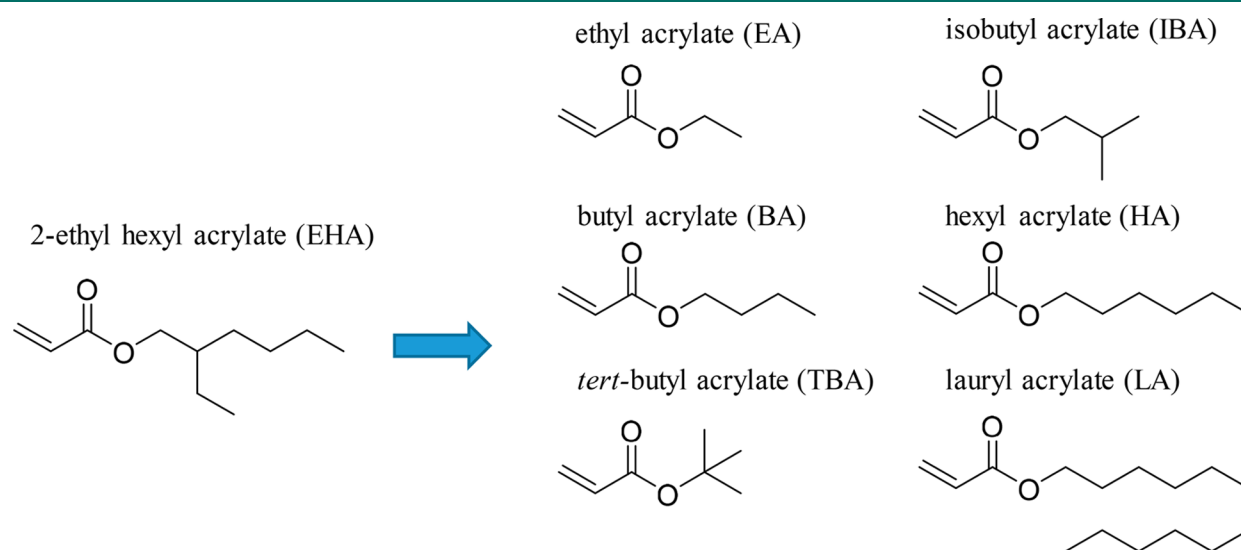
roughly the time normally required to thermally equilibrate a single sample. At each temperature, frequency sweeps are serially performed over all 48 samples, using a coaxial switching system to sweep through the samples prior to moving on to the next temperature. All of these steps are automated by a master LabView code. By parallelization of thermal equilibration and elimination of downtime between samples, this newly designed protocol realizes an order of magnitude improvement in the throughput of isothermal, equilibrium BDS measurements. Below we describe this new metrology and report results from

Table 2. Calculated Molar Masses Obtained by the GPC Spectra

sample no.	composition of inlet monomers (v:v)	M_w (g/mol)	M_n (g/mol)	$\bar{D} = M_w/M_n$
4	EHA	86325	65440	1.32
13	EHA:EA (70:30)	140379	109008	1.29
26	EHA:BA (75:25)	58595	46918	1.25
34	EHA:IBA (70:30)	110840	79772	1.39
46	IBA	131385	95990	1.37

parallel measurements of multiple test samples in comparison to those obtained via standard BDS measurements made on a commercially available instrument.

After validation of the instrument, this technique is applied to examine a series of acrylate-based statistical copolymers that are dielectrically active and readily copolymerizable in a range of compositions. We specifically probe interrelations among several figures of merit describing dynamics in glass-forming liquids^{28–30}—the glass transition temperature T_g , the kinetic fragility index m (which reflect the T_g -normalized thermal abruptness of the glass transition), and the stretching exponent β_{KWW} for non-exponential relaxation. Results for the composition dependence of T_g are consistent with the Fox equation for T_g values of



Binary Systems

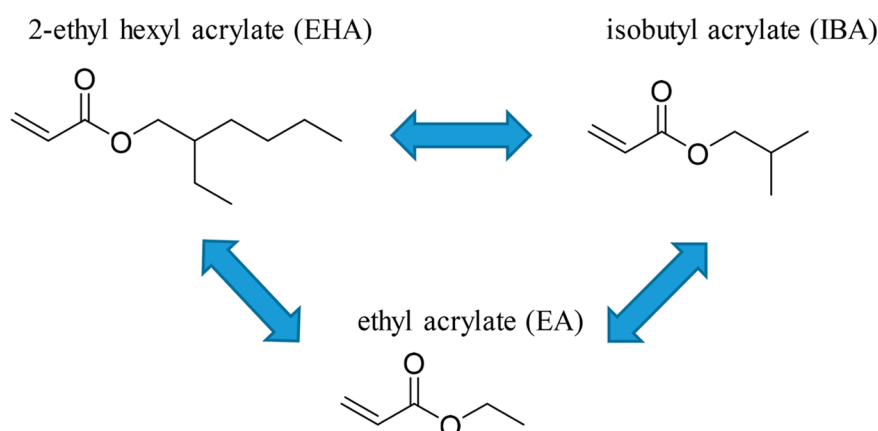


Figure 6. Chemical structures of monomers in the statistical copolymer systems.

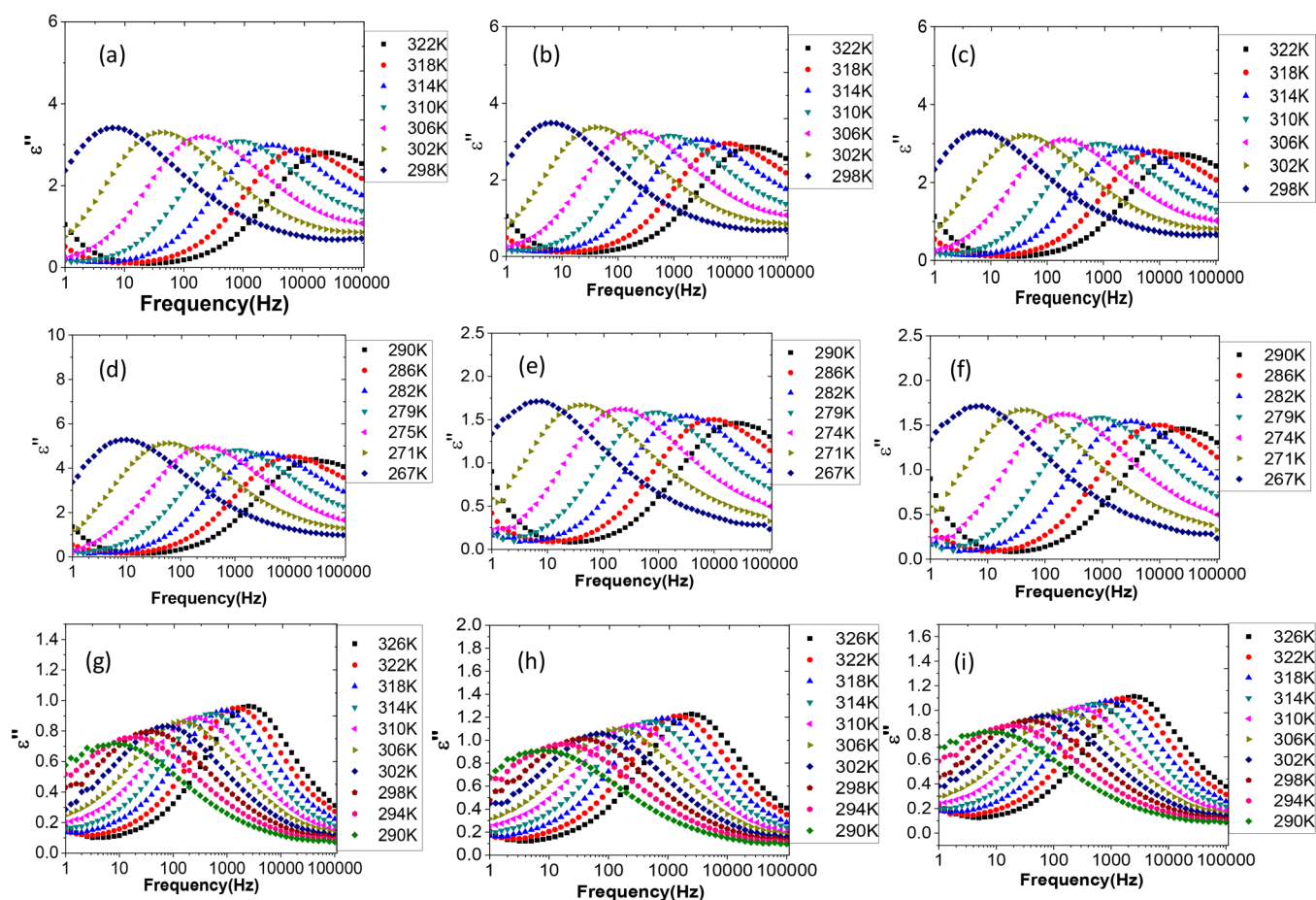


Figure 7. Sample dielectric-relaxation spectra obtained from the high-throughput measurements. The plots correspond to poly(methyl acrylate) on (a) switch 9, (b) switch 13, and (c) switch 15, poly(ethyl acrylate) on (d) switch 19, (e) switch 24, and (f) switch 30, and poly(2-ethylhexyl methacrylate) on (g) switch 37, (h) switch 41, and (i) switch 48.

multicomponent systems^{31–35}—a result consistent with the observation that near-unity reactivity ratios in these polymers tend to produce highly random monomer sequences that suppress confounding self-concentration effects.^{36–42} More broadly, the results suggest that, while there may be some correlation between T_g and the degree of relaxational stretching (β_{KWW}), neither of these quantities is well correlated with fragility of glass formation (m), in contrast to prior expectations in this field.

■ IMPLEMENTATION OF HIGH-THROUGHPUT BROAD-BAND DIELECTRIC SPECTROSCOPY

The HTBDS system consists of a temperature-control chamber, a dielectric interface, a dielectric analyzer, a parallel sample stage, and a coaxial switching system. The dielectric analyzer and interface are standard, commercially available instruments: a Solartron 1296A dielectric interface and 1260 impedance/gain-phase analyzer. These instruments are directly operated via the Solartron SMART software. The modifications enabling high-throughput operation consist of the custom parallel sample stage, custom coaxial switching system, environmental chamber (a Delta Design 9610 environmental chamber with a 9010 temperature controller), and associated custom LabView software for temperature control, coaxial switching control, and integration of dielectric measurements.

In a typical HTBDS experiment, 48 samples are prepared on distinct sample sites on the parallel sample stage. The sample

stage is then placed in the environmental chamber and connected to the coaxial switching system. The user configures the SMART software with the desired frequency-sweep experiment to be performed on each sample at each temperature and provides to a custom LabView program the set of temperatures to be assayed and thermal equilibration time to be employed after each temperature step. Once initiated, the environmental chamber equilibrates for the specified time at the initial temperature. The coaxial switching system then selects the first sample, after which an instance of a SMART software script that was preconfigured by the user is called to perform the specified dielectric measurement (typically an ac frequency sweep) on that sample. The LabView program then instructs the coaxial switching system to switch to the second sample, which is subject to the same dielectric measurement. This process is iterated under isothermal conditions until all 48 samples have been measured. The LabView program then instructs the environmental chamber to switch to the next temperature, thermally equilibrate for the specified time, and repeat this set of 48 measurements. The process is iterated until measurements have been made on all 48 samples at all the preset temperatures. The details of this process are provided below.

Parallel Sample Stage. In general, any dielectric sample holder consists of two electrodes separated by a gap space that contains the sample to be measured. A standard sample geometry for a BDS measurement of the type discussed here consists of two circular electrodes, approximately 3 cm in diameter,

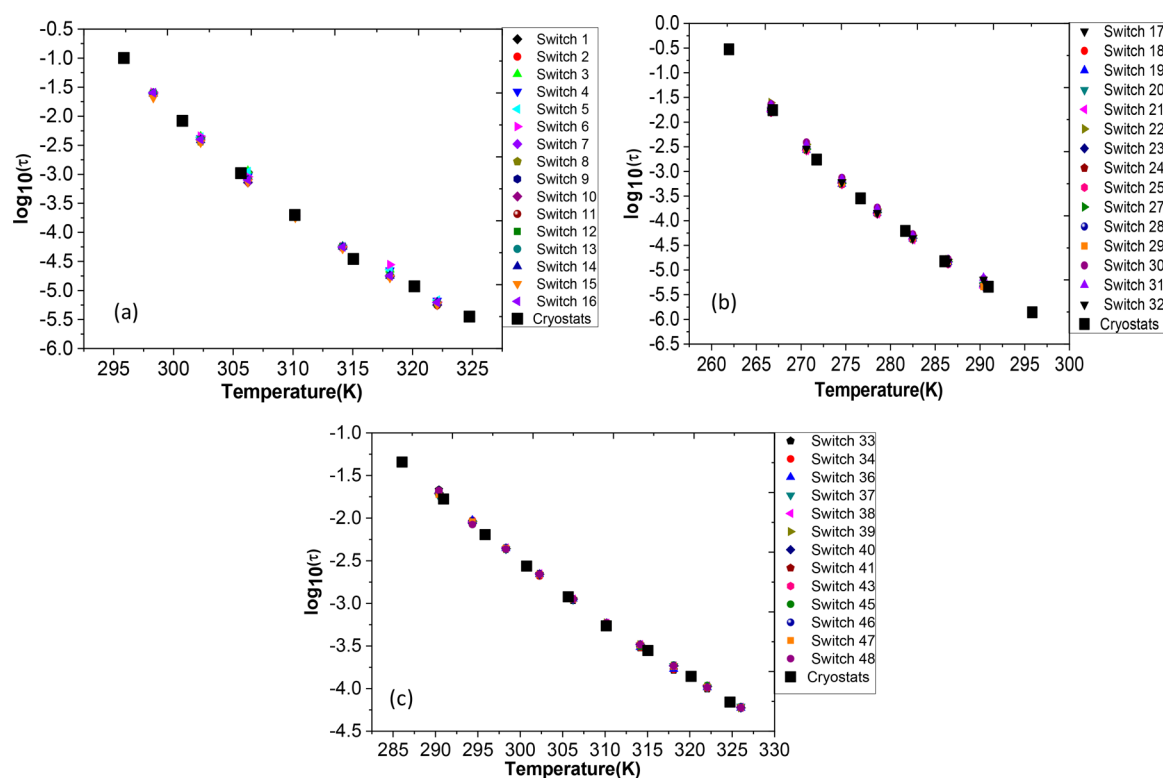


Figure 8. Arrhenius plots of the three polymers obtained from the high-throughput and commercially available setup. These plots correspond to (a) poly(methyl acrylate), (b) poly(methyl acrylate), and (c) poly(2-ethylhexyl methacrylate). Results from the cryostats are labeled with black squares. τ is in units of seconds.

separated by an approximately 50 μm thick sample film. Here we parallelize this sample geometry by arranging 48 such sample sites in a grid on a single stage. Sample selection is accomplished via a coaxial switching system applied to the upper electrode only. The sample baseplate provides a single ungated electrical pathway shared by all sample sites' lower electrodes.

The electrically shared sample baseplate, as shown by the schematic in Figure 1, consists of an aluminum testbed with dimensions of 25.72 cm $\times$ 33.92 cm $\times$ 1.05 cm. This testbed possesses 48 round pockets, each with a diameter of 3.18 cm and a depth of 0.15 cm. Each of these pockets holds a single removable sample capacitor, consisting of an approximately 50 μm thick sample film sandwiched between two identical brass disks. This spacing is maintained by employing 50 μm glass fiber spacers between the disks. Disks have a thickness of 0.32 cm, such that the lower disk in each capacitor protrudes 0.15 cm above the baseplate. Disks have a diameter of 3.18 cm, corresponding to a loose slip fit into the baseplate sockets, allowing for easy removal and cleaning after experiments. The baseplate is permanently attached to a single coaxial cable. Electrical contact between the capacitor and the baseplate is made mechanically, such that the baseplate serves as a shared bottom electrode for all samples.

The upper half of the stage provides distinct electrical pathways to each sample site to allow for independent measurement of each sample. As shown by the schematic in Figure 1b, the upper half of the stage consists of a glass plate with 48 drilled holes and 48 brass shafts. The 48 holes have the same center to center arrangement as the cavities on the baseplate. Each shaft is machined from brass rod stock into a cylindrical "T" shape. The head of each "T" forms a mechanical electrical contact with the corresponding sample capacitor. The shaft of each "T" protrudes

through one of the holes in the glass plate with a loose slip fit and is mechanically fixed with a coaxial cable: the core of the cable is inserted into a small hole in the top of the shaft and secured with a side pin. Each of these coaxial cables is then connected at its other end, via a SubMiniature version A (SMA) connection, to the coaxial switching system described below. Each brass shaft is also cuffed with a spring loaded between the head of the "T" and the glass plate.

All of the upper shafts are placed into contact with the corresponding sample capacitors simultaneously by aligning the corners of the glass plate and the corners of the testbed. The glass plate is kept in place and tightened by four clamps. The clamping forces between the glass plate and the testbed results in spring-loading forces on the shafts; these spring-loading forces ensure satisfactory contact between the shafts and sample capacitors.

We note that the brass disks used in the sample capacitors can also be employed in a standard commercially available sample stage, permitting for direct comparison between these methods. In both cases, the standard sample preparation is as follows. First, a layer of the sample film is solvent-cast onto a brass disk. The disks covered with solvent-cast films are vacuum-annealed overnight at 120 $^{\circ}\text{C}$ for solvent removal. Glass fibers (of 50 μm thickness) are then placed onto the sample to set a fixed capacitor gap size. Finally, an upper disk is placed to complete the dielectric capacitor. In this fashion, the 48 capacitors are placed and fitted into the pockets of the testbed.

Coaxial Switching and Dielectric Measurements. The switch system is designed such that only a single sample at any given time forms a closed electrical circuit with the dielectric interface, while other samples are isolated from the dielectric interface by open circuits. In this way, samples that are not being

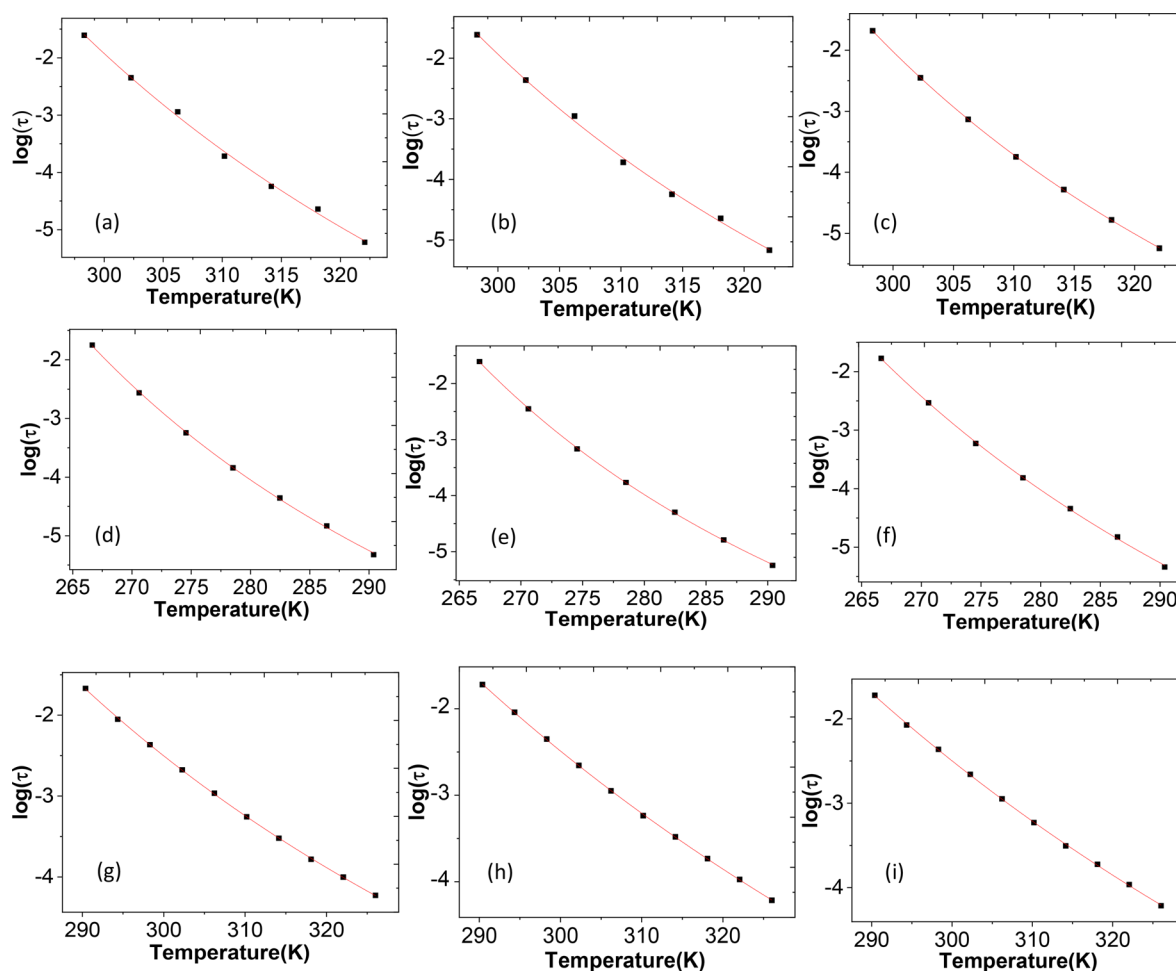


Figure 9. Sample relaxation time–temperature data obtained from the high-throughput measurements, with fits to the VFT form shown in red. These results correspond to (a) switch 3 (PMA), (b) switch 5 (PMA), (c) switch 15 (PMA), (d) switch 17 (PEA), (e) switch 1 (PEA), (f) switch 29 (PEA), (g) switch 33 (P2EM), (h) switch 41 (P2EM), and (i) switch 45 (P2EM).

Table 3. Statistics of T_g and m Obtained from Different Sites

		average	standard deviation	cryostat
poly(methyl acrylate)	T_g (K)	284.7	0.50	286.2
	m	96.8	4.97	111.0
poly(ethyl acrylate)	T_g (K)	253.1	0.80	254.0
	m	92.6	6.13	98.4
poly(2-ethylhexyl methacrylate)	T_g (K)	257.1	1.53	257.2
	m	36.7	2.40	37.3

measured do not interfere with the rest of the samples. Dielectric measurements of different samples are conducted consecutively and automatically using the switching system before the environmental chamber moves on to the next set point temperature.

The switch system consists of three major remote modules that connect switches corresponding to the upper electrodes of different samples. The control system consists of a 34980 multi-function switch/measure unit by Keysight (the controller) and ten coaxial switches from Agilent.⁴³ The controller connects to the switches by a 34945 EXT remote module. To test the 48 samples, ten coaxial switches are connected to two remote modules. The master remote module has eight switches controlled, and the slave remote module has two. Each switch has 4/6 channels, and the channel numbering of the switch is determined by the bank and slot numbers of the EXT remote

module. While the upper electrodes are interconnected with remote switches, all of the samples share the same lower electrode. Each sample corresponds to several switch channels. As shown in Figure 2, the input signal goes through the first switch and can go to the #4 switch and then the #9 switch. For example, if sample 37 needs to be tested, then switch channels 1106, 1135, and 1201 must be closed simultaneously.

For each sample, frequency sweeps are performed using a 1260 impedance/gain-phase analyzer and a 1296 dielectric interface, which were purchased from Solartron Inc.⁴³ Data collection and interpretation were performed using SMART software during each frequency sweep. The internal reference mode was applied for the high-frequency-range testing, while the normal mode was applied in the low-frequency range. After a frequency sweep was finished for a sample of interest, the coaxial switch systems automatically dialed for the next sample.

LabVIEW Program. An entire HTBDS measurement consists of the following protocol. First, the environmental chamber equilibrates at the initial temperature; this temperature is maintained until the equilibration time is reached. The dielectric interface and the impedance analyzer then start to conduct dielectric measurements at this particular temperature; the SMART program automatically starts and saves the data file. After a measurement is finished for a particular sample, the measurement of the next sample is conducted.

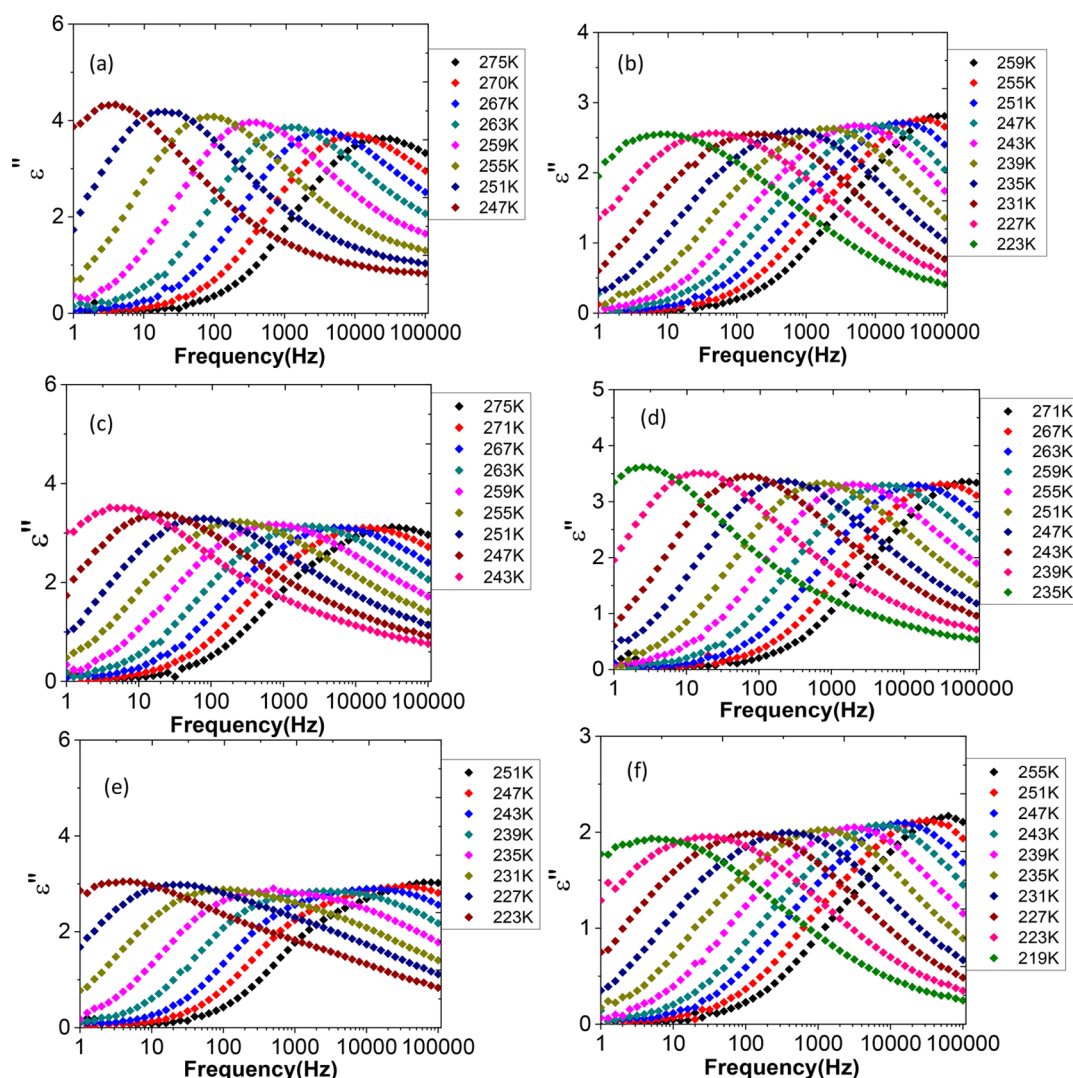


Figure 10. Sample dielectric-relaxation spectra obtained from measuring binary statistical copolymer systems using the HTBDS. The plots correspond to EHA-based copolymer containing weight fractions of (a) 0.6 EA, (b) 0.15 BA, (c) 0.3 TBA, (d) 0.45 IBA, (e) neat HA, and (f) 0.3 LA.

Once the measurements of all the selected samples are completed, the environmental chamber moves to the next temperature through a step change; this entire process is then repeated, as shown in Figure 3. The process is automated by a custom LabVIEW program.

The LabView program accepts the following parameters: initial temperature, final temperature, temperature step change, equilibration time, and sample numbers. The program begins by setting the environmental temperature set point to its initial temperature and waiting the specified equilibration time for this temperature to stabilize. Details on equilibration time determination are discussed in the next section. The LabView program then runs a preconfigured instance of the Solartron Smart software, which conducts specified dielectric measurements on the first sample. In this step, the program will command the switch system to close the circuit on the measured sample while other switches set to open circuits. After one sample is finished, the LabView program switches the closed circuit to the next sample and again calls the Smart software script. This is repeated until all samples are measured. Upon completing the frequency sweeps of all the designated samples, the program commands the temperature chamber to move on to the next temperature and repeat this process until measurements are finished on the final temperature.

Temperature Control and Calibration. The temperature of all 48 samples is controlled simultaneously by a Delta Design 9610 environmental chamber with a 9010 temperature controller.⁴³ The testbed is placed in the middle of the chamber. Cooling is performed via liquid nitrogen. Compressed dry nitrogen is constantly purged into the chamber. This equipment has a National Institute of Standards and Technology (NIST) traceable calibration certificate obtained by Cal Tech. We determined the equilibration time by measuring the sample stage temperature in situ using thermocouples.

Temperature calibration was performed using an Applent AT4610 Multi-Channel Temperature Meter,⁴³ with a NIST-traceable calibration certificate obtained by Cal Tech. We embedded these thermocouples between the two electrodes and generated the temperature vs time curve (shown in Figure 4) by recording the temperature and time through a 5 K step change. As shown in the figure, we used two channels (channel 01 and channel 10). Channel 01 measures the ambient temperature inside the Delta Design chamber,⁴³ while channel 10 measures the temperature of the sample stage. The temperature vs time curve (Figure 4b) illustrates that the time corresponding to the 1/e value of the 5 K step change is around 20 min. We therefore employ a 40 min temperature-equilibration time to

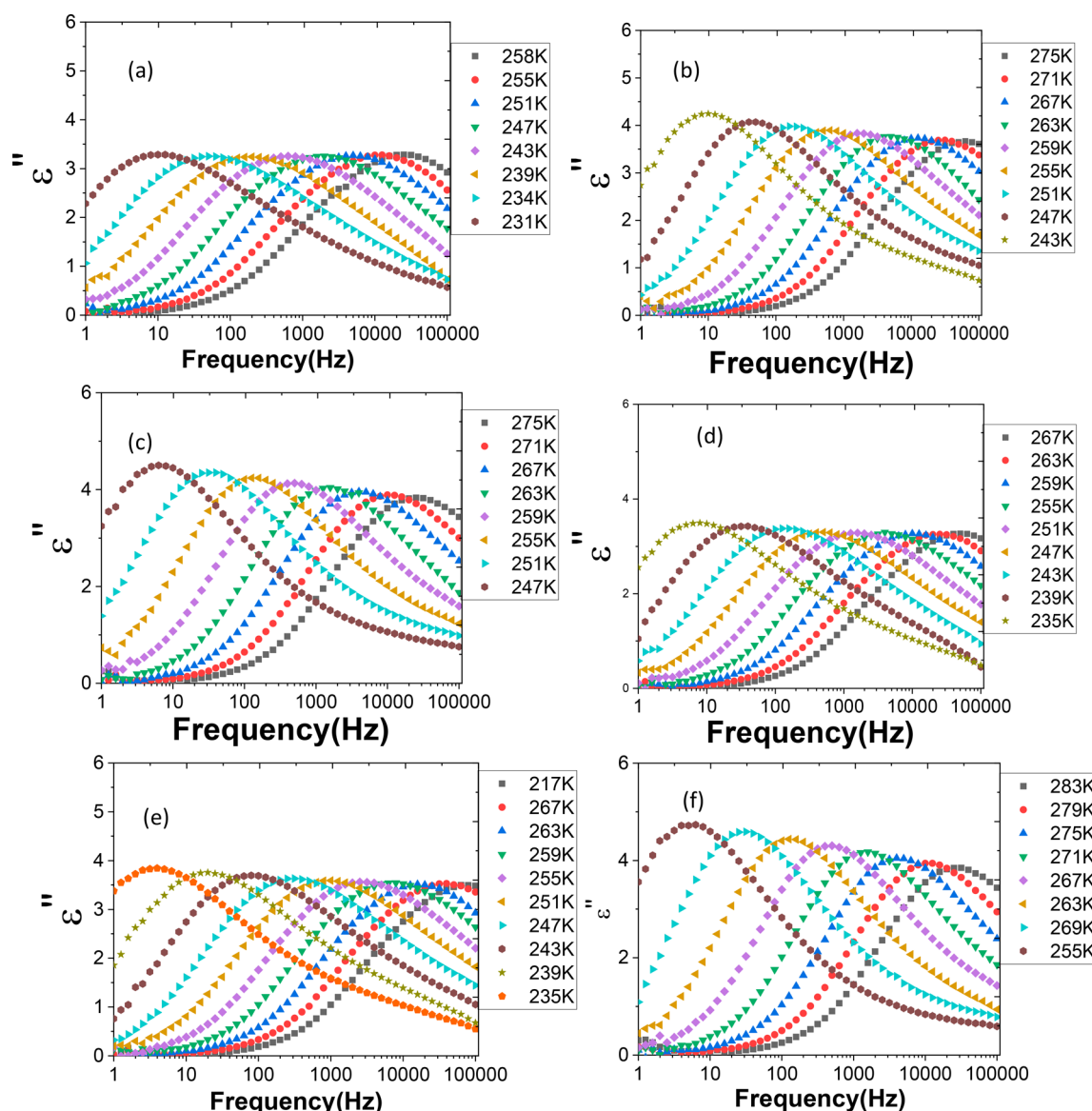


Figure 11. Sample dielectric-relaxation spectra obtained from measuring ternary statistical copolymer systems using the HTBDS. The plots correspond to ternary copolymer systems containing the following monomer compositions: (a) 0.75 EHA, 0.125 IBA, 0.125 IBA; (b) 0.25 EHA, 0.25 IBA, 0.25 IBA; (c) 0.375 EHA, 0.375 IBA, 0.25 EA; (d) 0.625 EHA, 0.25 IBA, 0.125 EA; (e) 0.625 EHA, 0.125 IBA, 0.25 EA; (f) 0.125 EHA, 0.625 IBA, 0.25 EA.

ensure that the temperature is in a steady state during the dielectric measurements. The recorded temperatures for the 48 samples are based on a linear interpolation of the NIST-traceable calibration performed on the environmental chamber.

TEST MATERIALS

Commercially Available Polymers for Validation. The HTBDS instrument was validated by testing three polymers: poly(methyl acrylate) (PMA), with mass average relative molar mass (M_w) $\cong$ 40 kg/mol, poly(ethyl acrylate) (PEA), with M_w $\cong$ 95 kg/mol, and poly(2-ethylhexyl methacrylate) (P2EM), with M_w $\cong$ 123 kg/mol. All of the tested polymers were purchased in solution form from Sigma-Aldrich, without further purification.⁴³ The molecular structures of these polymers are shown in Figure 5. All possess substantial internal dipole moments, making them suitable for BDS measurements.

All of the polymers in their original solution forms were drop-cast onto brass disks and vacuum-dried overnight for solvent removal. Sample capacitors were then completed by placing

glass fibers on each sample followed by placement of the upper electrode. We made 16 sample capacitors for each polymer, with poly(methyl acrylate), poly(ethyl acrylate), and poly(2-ethylhexyl methacrylate) on the testbed pockets corresponding to switches 1–16 (the first two rows on the testbed), switches 17–32 (the two middle rows), and switches 33–48 (the two bottom rows), respectively. The stage was then assembled and placed into the environmental chamber. The input parameters for the LabVIEW programs are shown in Table 1. For the frequency sweep, we selected the frequency range to be $1\text{--}10^6$ Hz, with 10 data points per decade. The dielectric interface was operated using the internal reference mode for noise reduction. The temperature range was selected such that segmental relaxation peaks could be observed in the selected frequency regime. An LC 230 22 PSI low-pressure liquid nitrogen Dewar, purchased from Praxair, was used for cooling. Compressed nitrogen, used as a protective gas, was continuously fed into the chamber to create a moisture- and oxygen-free environment inside the chamber.

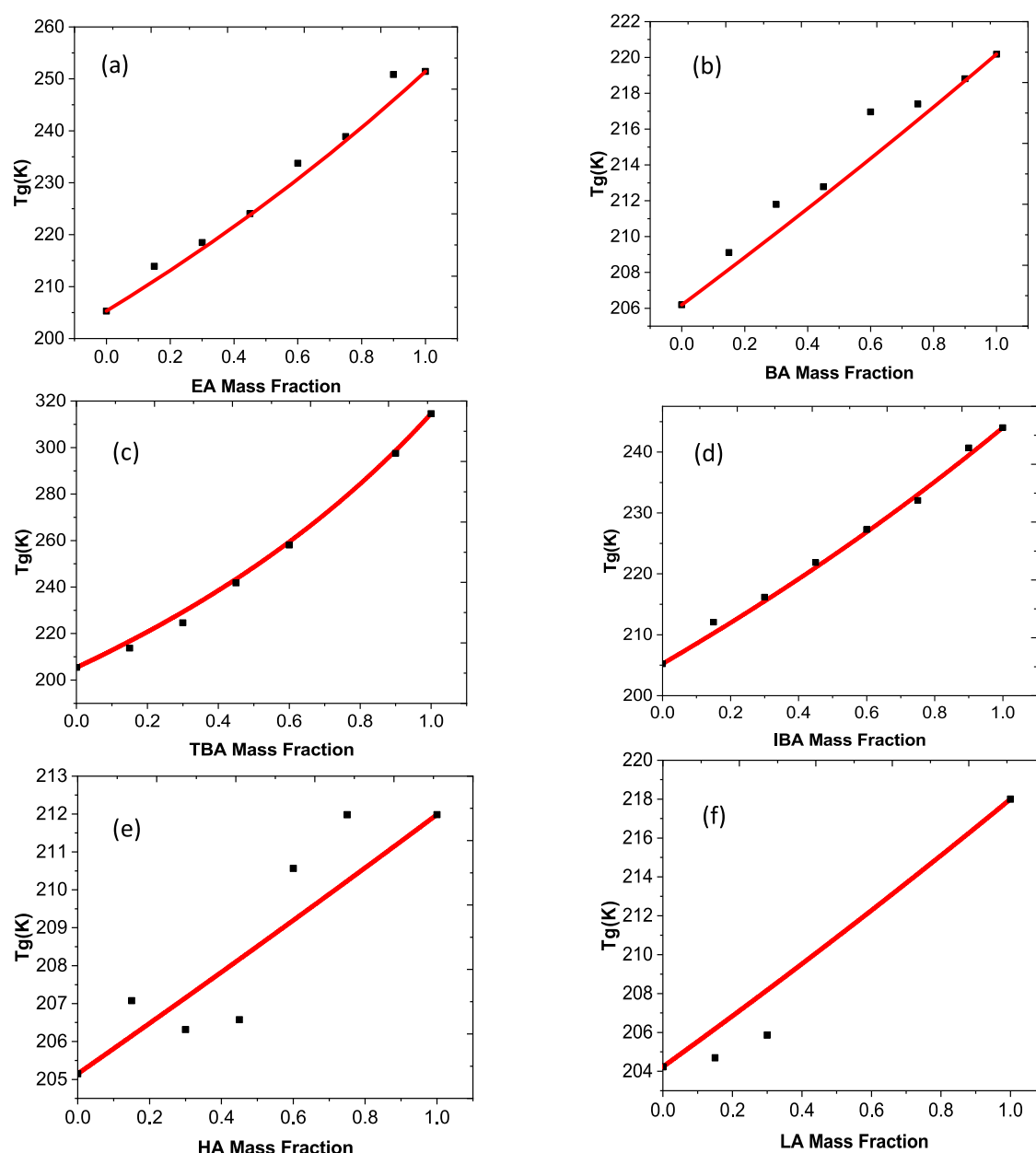


Figure 12. Dielectric T_g values of EHA-based statistical copolymer systems containing monomers of (a) EA, (b) BA, (c) TBA, (d) IBA, (e) HA, and (f) LA. The standard errors for the T_g as a VFT fit parameter to relaxation data are smaller than the data points.

Upon completion of the HTBDS testing, we ran samples of each material on the commercial BDS setup for comparison, using Super Tran Series continuous-flow variable-temperature cryostats, purchased from Solartron.⁴³ Here, we disassembled the HTBDS setup and chose three capacitors of each sample to conduct measurements on the cryostats. The protocol for the temperature sweep was the same as that used in HTBDS. A broader frequency range was chosen for these serial measurements (10^{-1} – 10^6 Hz). The set point temperatures on the cryostats were corrected on the basis of the real-time data collected from the Applent AT4610 Multi-Channel Temperature Meter.⁴³ These temperatures were further corrected using the NIST-traceable calibration certificate.

Between uses, we applied the following procedures for cleaning the brass disks. First, we placed the used capacitor onto a specially machined metal block equipped with a pocket with the same dimension of the pockets on the testbed. We heated

the block along with the used sample capacitor on a hot plate for 30 min. After the viscosity of the old sample was sufficiently reduced upon melting, we removed the top brass disk with a C-shaped metal tool while the bottom disk stayed in the metal block. Upon separating the old capacitors into individual disks, we immersed the disks into a beaker containing solvent to wash off the polymer on the disks several times. With the residual polymers removed thoroughly, these disks were polished with 3 M polishing papers using CRC industrial penetrating oil as lubricant. Finally, we washed off the industrial oil with acetone and water.

Binary and Ternary Statistical Copolymers. We next applied the HTBDS technique to investigate a series of binary statistical copolymer systems using ethylhexyl acrylate as the base monomer. These copolymer systems were synthesized by copolymerizing (2-ethylhexyl acrylate (EHA) monomer with six types of acrylate monomers: ethyl acrylate (EA), butyl acrylate (BA), *tert*-butyl acrylate (TBA), isobutyl acrylate (IBA), hexyl

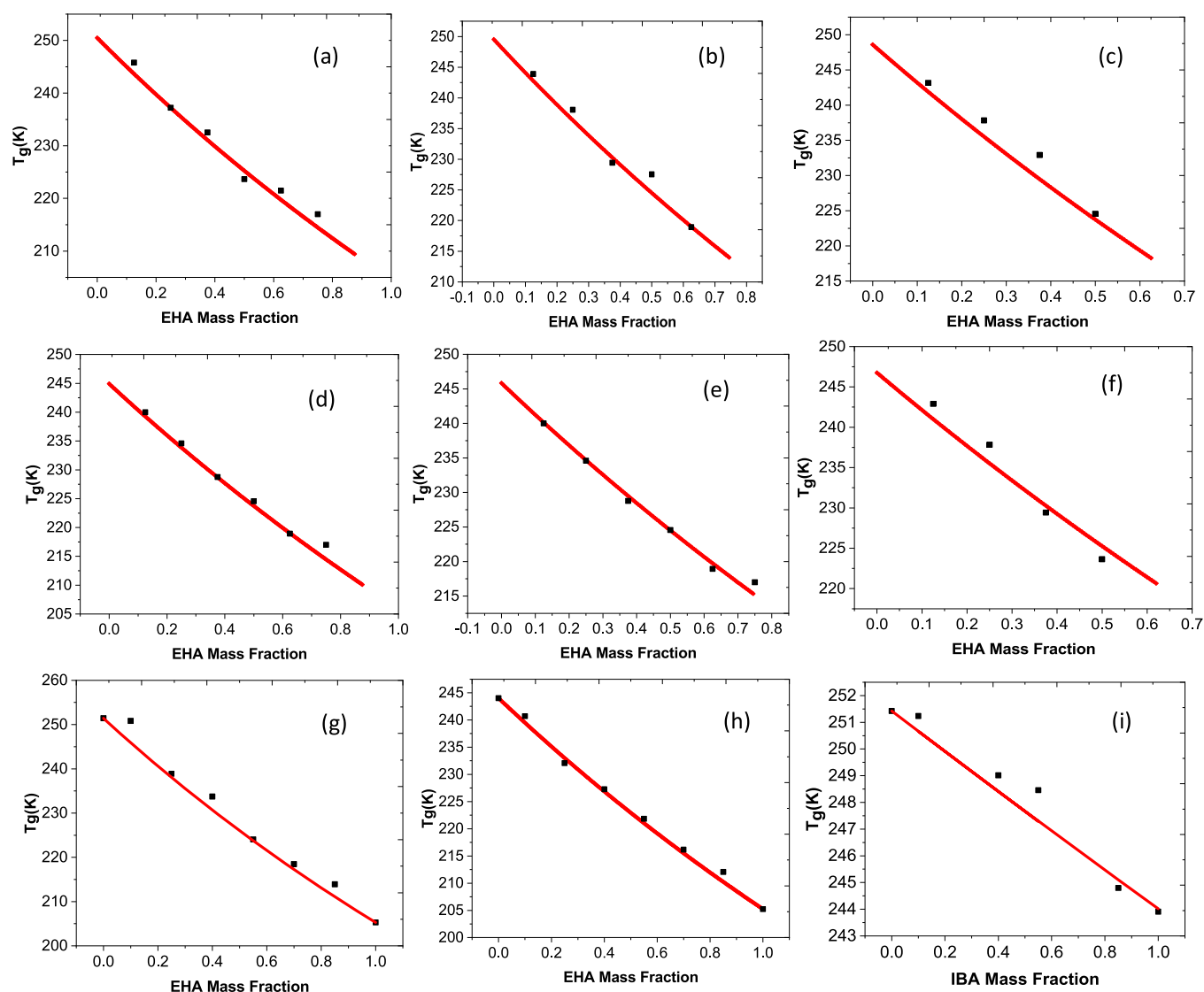


Figure 13. Dielectric T_g values of EHA-IBA-EA ternary copolymer systems containing (a) 0.125 IBA, (b) 0.25 IBA, (c) 0.375 IBA, (d) 0.125 EA, (e) 0.25 EA, (f) 0.375 EA, (g) 0 IBA, (h) 0 EA, and (i) 0 EHA.

acrylate (HA), and lauryl acrylate (LA). Among the six binary copolymer systems, the selected mass fractions of a specific monomer were 0 (pure EHA), 0.15, 0.3, 0.45, 0.6, 0.75, 0.9, and 1. In addition to binary systems, we also synthesized and measured a series of ternary copolymer systems based on EHA, IBA, and EA. Chemical structures of these monomers are shown in Figure 6.

Chlorobenzene (99%, Alfa Aesar) and methanol ($\geq 99.8\%$, VWR International) were used as received. *n*-Ethyl acrylate (99%, Sigma-Aldrich), *n*-butyl acrylate ($>98.0\%$, Sigma-Aldrich), *tert*-butyl acrylate (98%, Sigma-Aldrich), isobutyl acrylate ($\geq 99\%$, Sigma-Aldrich), hexyl acrylate (98%, Sigma-Aldrich), 2-ethylhexyl acrylate (98%, Sigma-Aldrich), and lauryl acrylate (96%, Sigma-Aldrich) were purified by passing through a basic alumina column to remove the hydroquinone inhibitor before use. Benzyl dodecyl trithiocarbonate (BDTC), a nonionic RAFT agent, was synthesized by a previously reported method. 2,2'-Azobis(2-ethylpropionitrile) (AIBN, Sigma-Aldrich) was purified by dissolving in methanol at 45°C and recrystallizing in a freezer.^{43,44}

RAFT Copolymerization by High-Throughput Polymerization Robot. A custom-built high-throughput polymerization robot (J-Kem Scientific) was used for reversible

addition–fragmentation chain transfer (RAFT) polymerization. Monomer solutions were performed in chlorobenzene (mass:mass = 50:50) in 20 mL scintillation vials purged with nitrogen gas. A RAFT solution composed of 4 mmol of BDTC and 0.8 mmol of AIBN in 10 g of chlorobenzene was prepared as well. All of the reagents mentioned above were located on the reagent rack (a maximum of 50 monomer solutions could be accommodated on this 10 rows $\times$ 5 columns rack). A syringe pump mounted on an *x-y-z* stage was programmed to transfer a designated amount of monomer solutions from the reagent rack to each of 48 nitrogen-charged reaction vials (8 mL) located on the two hot plates, each equipped with a 6 rows $\times$ 4 columns aluminum heating block. The syringe pump provided reliable volume measurements within 0.01 mL. After the distribution of monomer solutions by the robot was finished, the reactions were performed at 65°C for 12 h. The polymerizations were stopped by cooling the reaction vials with cold water. A small portion of chlorobenzene was removed in the vacuum oven at 80°C for 12 h. Unreacted monomers could be separated by addition of methanol as a poor solvent to precipitate the polymer. After redissolution in solvent and precipitation with methanol,

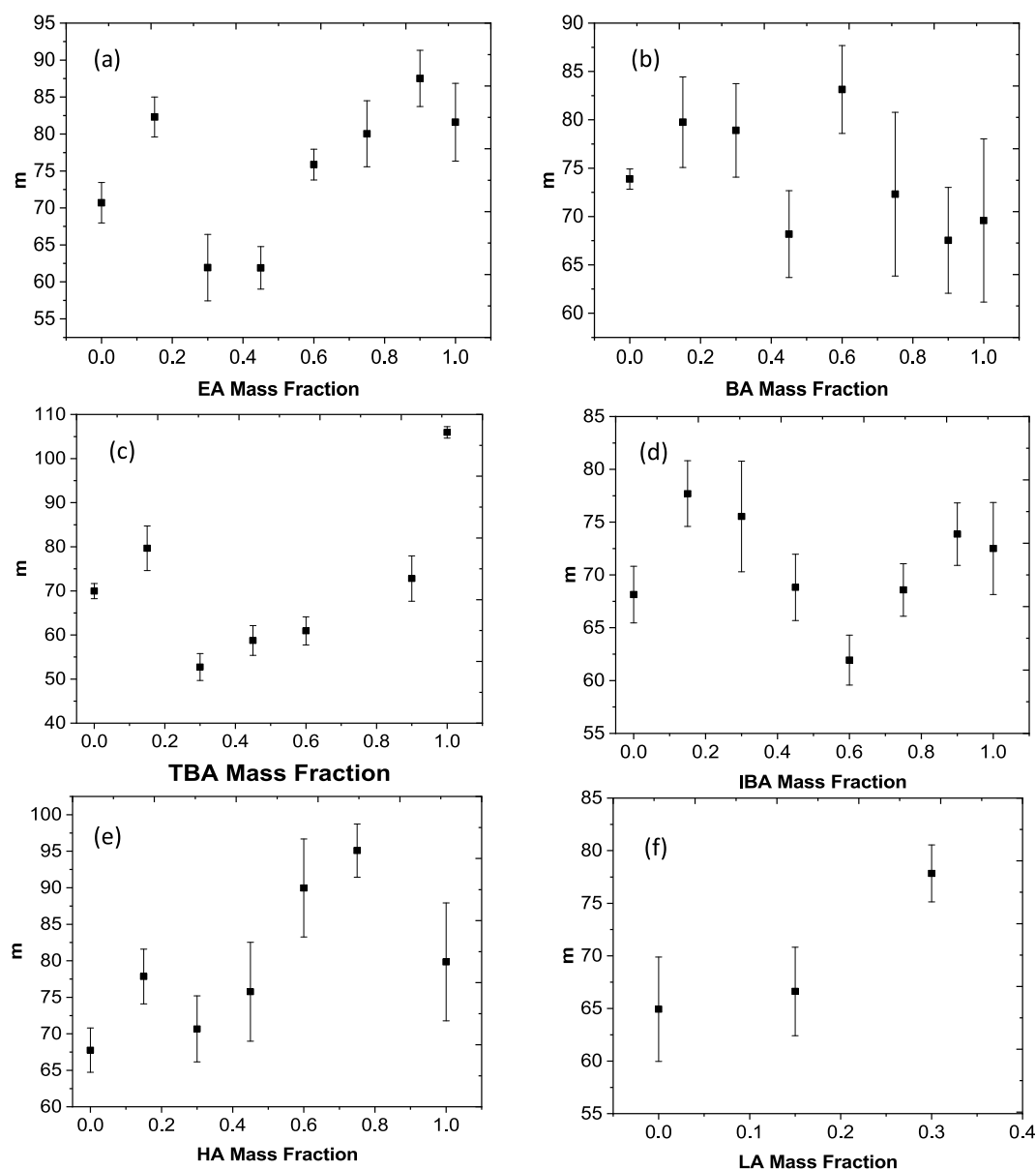


Figure 14. Fragility index values of EHA-based statistical copolymer systems containing monomers of (a) EA, (b) BA, (c) TBA, (d) IBA, (e) HA, and (f) LA. Error bars are standard errors for m as a VFT fit parameter.

polymers were transferred to the vacuum oven to remove the trapped solvent residue at 65 °C for 24 h.

Randomly selected polymers were analyzed by ^1H nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC). ^1H NMR spectra were collected on a Varian Mercury 300 MHz spectrometer. The ^1H NMR spectra of five randomly selected polymers (see Figures S1–S5 in the Supporting Information) showed that the characteristic chemical shifts of unreacted monomers (Figure S6 in the Supporting Information: 6.33–6.59 ppm, $-\text{CH}=\text{CH}_2$; 5.71–6.26 ppm, $\text{CH}_2=$) were absent. Molar masses were analyzed on a Waters Breeze System SEC instrument equipped with three Water Styragel columns and a Waters 2414 refractive index detector (RI). The SEC measurements were carried out in tetrahydrofuran as eluent at 35 °C. The SEC spectra of five randomly selected polymers revealed the actual molar masses (number-average molar masses $M_n \approx 47$ –140 kg/mol, $D \approx 1.2$ –1.3) calculated from the calibrated polystyrene standards, as shown in Table 2.

RESULTS AND DISCUSSION

Instrument Validation. A major application of BDS is the characterization of relaxation dynamics in glasses and glass-forming liquids such as the polymers considered here. Relaxation behavior is commonly quantified on the basis of the dielectric loss ϵ'' —the imaginary part of the complex dielectric permittivity ϵ^* determined from the measured complex capacitance $C^* = \frac{\epsilon^* \epsilon_0 A}{d}$, where ϵ_0 is the permittivity of free space (8.854 pF/m), A is the electrode diameter, and d is the sample thickness. ϵ'' quantifies the dissipative component of dipole relaxation in response to a low-amplitude ac electrical field. Peaks in this quantity with respect to temperature correspond to relaxation processes on a frequency comparable to the peak frequency. Representative dielectric spectra obtained via HTBDS are shown in Figure 7. The spectra obtained from other switches are comparable to those shown here. The smooth relaxation peaks visible on these spectra indicate that the signal

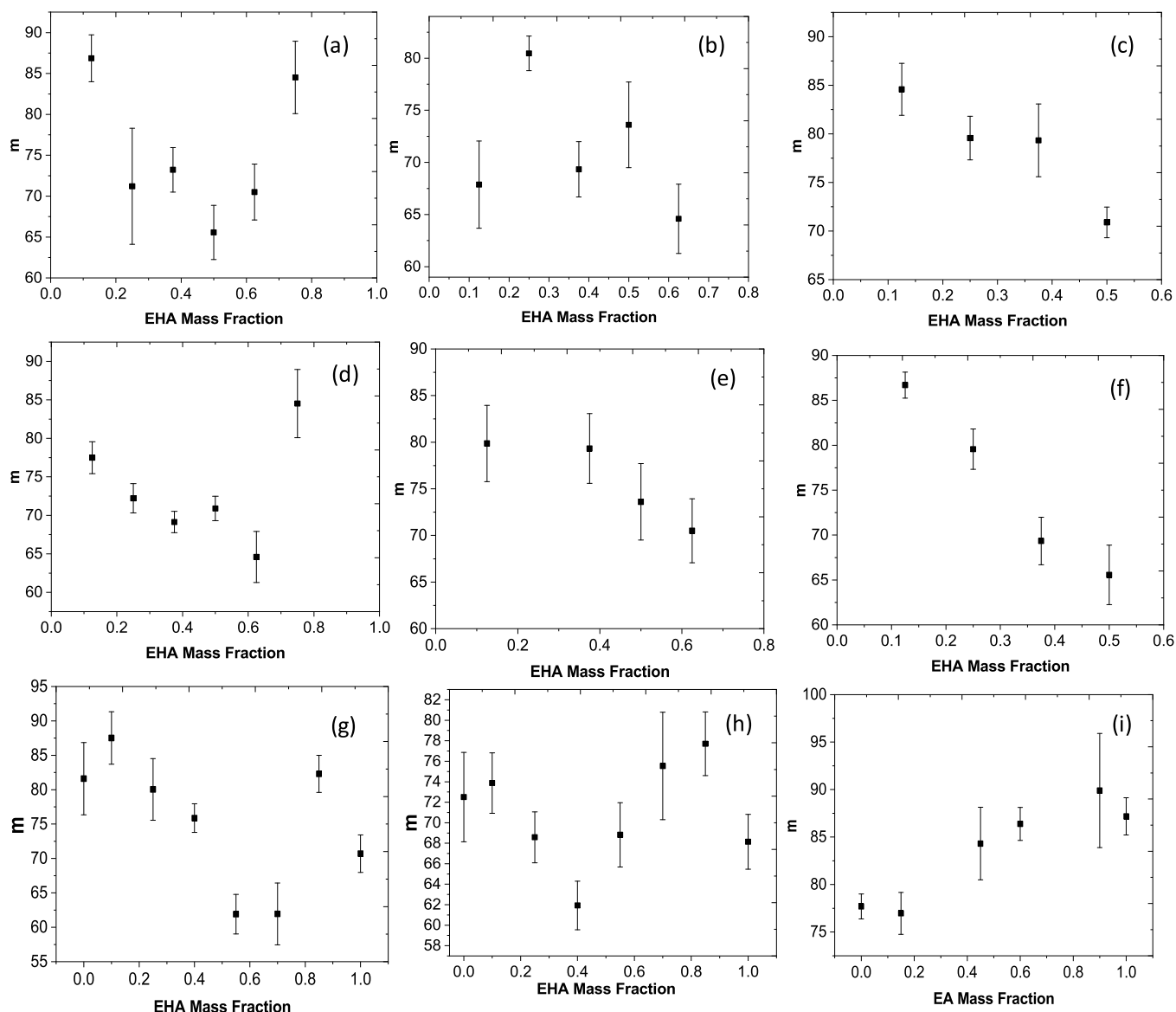


Figure 15. Dynamic fragility, $m(\tau = 100 \text{ s})$ values of EHA-IBA-EA ternary copolymer systems containing (a) 0.125 IBA, (b) 0.25 IBA, (c) 0.375 IBA, (d) 0.125 EA, (e) 0.25 EA, (f) 0.375 EA, (g) 0 IBA, (h) 0 EA, and (i) 0 EHA. Error bars are standard errors for m as a VFT fit parameter to each relaxation time data set.

to noise ratio on the HTBDS was acceptable for these types of measurements. As shown by Figure 8, distinct sample capacitors yield comparable results for samples of the same composition.

In order to further verify site to site reproducibility and data quality, we extracted a temperature-dependent segmental relaxation time, τ_{ω} for each sample. The dielectric loss peaks were fit with the Havriliak–Negami function, as shown in eqs 2–5:^{45–47}

$$\epsilon^* = \epsilon' + i\epsilon'' \quad (2)$$

where:

$$\epsilon'(\omega) = \epsilon_s + \Delta\epsilon \left[1 + 2(\omega\tau_{\text{HN}})^m \cos\left(\frac{\pi m}{2}\right) + (\omega\tau_{\text{HN}})^{2m} \right]^{-n/2} \cos(n\phi) \quad (3)$$

$$\epsilon''(\omega) = \Delta\epsilon \left[1 + 2(\omega\tau_{\text{HN}})^m \cos\left(\frac{\pi m}{2}\right) + (\omega\tau_{\text{HN}})^{2m} \right]^{-n/2} \sin(n\phi) \quad (4)$$

where:

$$\phi = \tan^{-1} \left[\frac{(\omega\tau_{\text{HN}})^m \sin\left(\frac{\pi m}{2}\right)}{1 + (\omega\tau_{\text{HN}})^m \cos\left(\frac{\pi m}{2}\right)} \right] \quad (5)$$

Here, $\Delta\epsilon$ is the dielectric strength, which is the difference between the static ϵ_s and instantaneous ϵ_i dielectric constants, τ_{HN} is the Havriliak–Negami relaxation time, and n and m are shape parameters. The relaxation time τ was determined from these HN fits as

$$\tau = \frac{1}{2\pi f_{\text{max}}} \quad f_{\text{max}} = \frac{1}{2\pi\tau_{\text{HN}}} \left[\frac{\sin\left(\frac{\pi m}{2+2m}\right)}{\sin\left(\frac{\pi m}{2}\right)} \right]^{1/n} \quad (6)$$

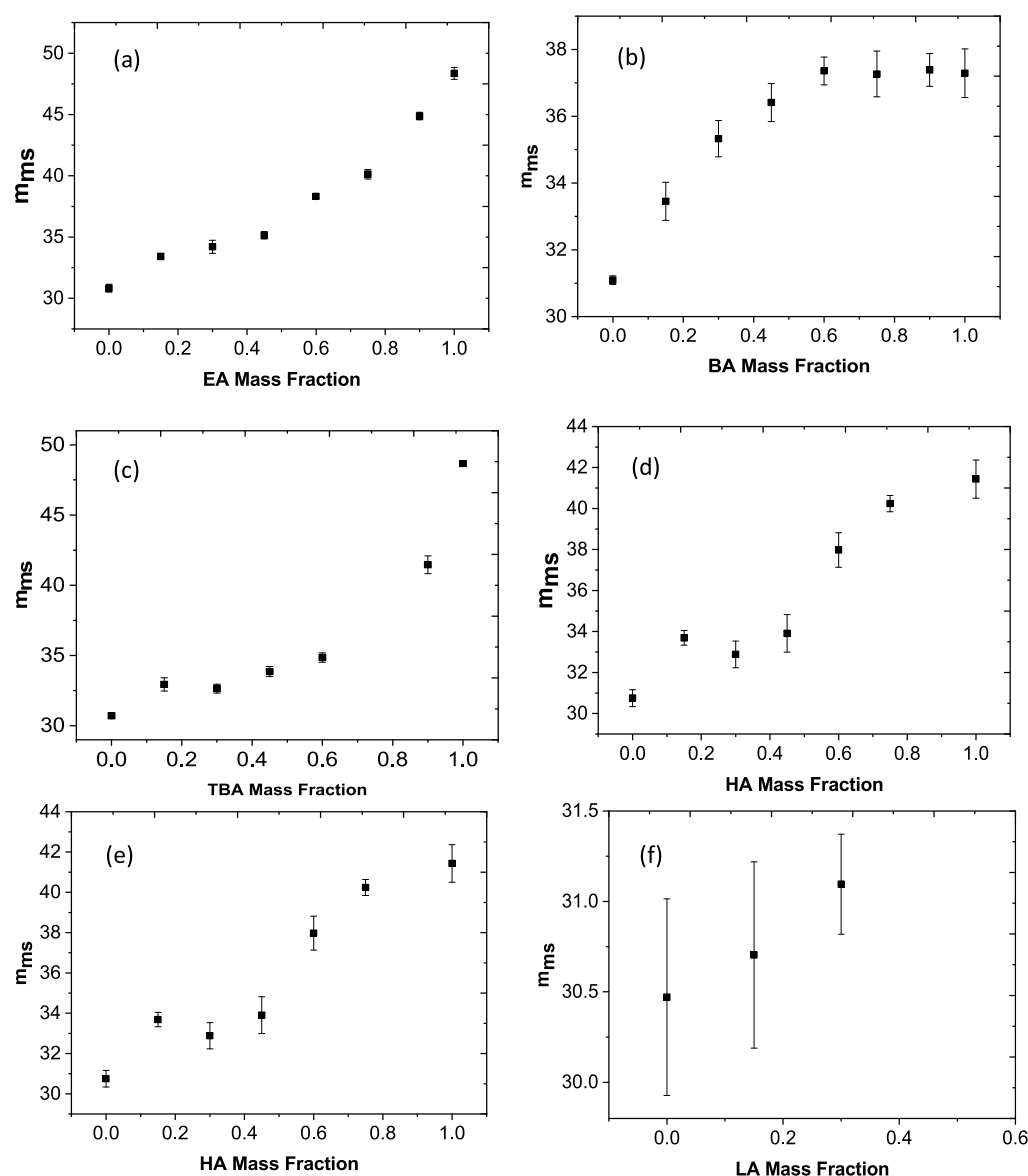


Figure 16. Millisecond fragility values (m_{ms}) of EHA-based statistical copolymer systems containing monomers of (a) EA, (b) BA, (c) TBA, (d) IBA, (e) HA, and (f) LA. Error bars are standard errors for m as a VFT fit parameter to each relaxation time data set.

Relaxation times for these samples are plotted in Figure 8 vs temperature. The failure rate for this batch was 4 out of 48 samples, which was caused by human errors during the sample preparation leading to short circuits or insufficient electrical contact. This failure rate is similar to that of the conventional setup. Notably, data collected from different sample sites are in excellent agreement with each other and with data from the commercially available cryostat-controlled sample stage. This agreement indicates that HTBDS and the conventional BDS yield equivalent results, with the exception of a truncation of the lowest frequencies in the HTBDS measurement to accommodate high-throughput measurement.

These relaxation data were further fit with the Vogel–Fulcher–Tammann (VFT) equation⁴⁵ to extract the glass transition temperature T_g and kinetic fragility index m . The former figure of merit reports on the temperature at which the system's segmental relaxation time exceeds some experimental time scale, commonly defined by convention as 100 s. The latter is defined as

$$m = \left. \frac{d \log \tau}{d(T_g/T)} \right|_{T=T_g} \quad (7)$$

This quantity reports on the extent to which the relaxation dynamics of the material deviate from those of an Arrhenius rate law, with a value of 16–17 generally corresponding to Arrhenius dynamics and with the most fragile (strongly non-Arrhenius) glass forms known exhibiting values greater than 300.⁴⁸ Practically, m is also closely related to the thermal abruptness of the transition⁴⁹ and thus is a central determinant of thermal processing windows and of mechanical response above T_g .

Here we employ a form of the VFT equation that has been recast in terms of T_g and m :

$$\log \tau = \log \tau_0 + \log \left(\frac{\tau_g}{\tau_0} \right) \times \left[\frac{T}{T_g} + \left(\frac{m}{\log \left(\frac{\tau_g}{\tau_0} \right)} - 1 \right) \left(\frac{T}{T_g} - 1 \right) \right]^{-1} \quad (8)$$

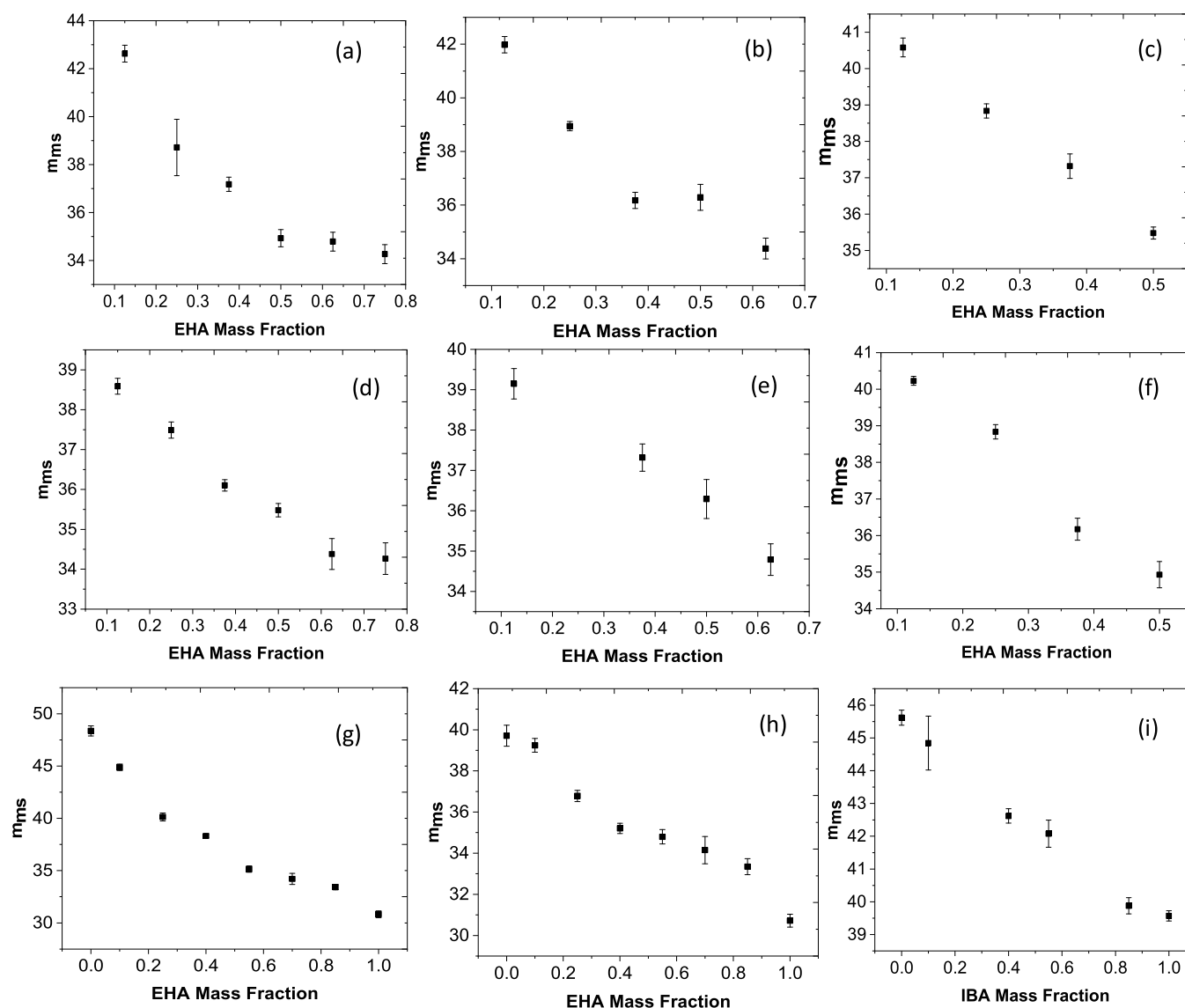


Figure 17. Millisecond fragility values (m_{ms}) of EHA-IBA-EA ternary copolymer systems containing (a) 0.125 IBA, (b) 0.25 IBA, (c) 0.375 IBA, (d) 0.125 EA, (e) 0.25 EA, (f) 0.375 EA, (g) 0 IBA, (h) 0 EA, and (i) 0 EHA. Error bars are standard errors for m as a VFT fit parameter to each relaxation time data set.

where τ_0 is an extrapolated high-temperature relaxation time and where we define the relaxation time τ_g at the glass transition to be equal to 100 s.

As shown by Figure 9, the samples' relaxation behavior conforms to the VFT form, as expected. Results from distinct switches again yield consistent results. As shown by Table 3, values of T_g and m obtained from distinct sites are in excellent agreement, with standard deviations in the range of 1–2 K for T_g and 1–4 dimensionless units for m . This uncertainty range is typical for results obtained from VFT fits with 7–10 decades of relaxation as obtained via conventional BDS.^{24,50} The results from HTBDS exhibit minor deviations from those obtained in the cryostat single-sample stages—a consequence of the broader range of frequencies probed in the cryostat experiments.

The entire set of HTBDS measurements required approximately 65 h. A measurement of a single sample in the commercial sample stage requires approximately 20 h, such that performing all of these measurements serially would have required approximately 960 h, or 40 days of continuous measurement. The HTBDS thus realized nearly a 15-fold reduction in measurement time for

48 samples in comparison to the single-sample measurements. Given the difficulty of arranging continuous 20 h measurements from a human time standpoint, the practical throughput improvement of these measurements is likely higher.

Investigation of Binary and Ternary Statistical Copolymers. With the HTBDS validated, we now consider the dynamics and glass formation behavior of the set of statistical acrylate copolymers described in the methods section. We specifically consider copolymers of ethylhexyl acrylate (EHA) with 6 comonomers: ethyl acrylate (EA), butyl acrylate (BA), *tert*-butyl acrylate (TBA), isobutyl acrylate (IBA), hexyl acrylate (HA), and lauryl acrylate (LA). In each case, we consider 8 distinct copolymer mole fractions, with each series including the case of an EHA homopolymer and a homopolymer of the selected copolymer. This yields a total of 48 systems, corresponding to the 48-sample capacity of the HTBDS. These 48 samples include 6 samples of EHA homopolymer, providing an additional layer of instrument validation. In addition to the binary polymer systems, we also investigated a series of EHA-EA-IBA ternary copolymer systems.

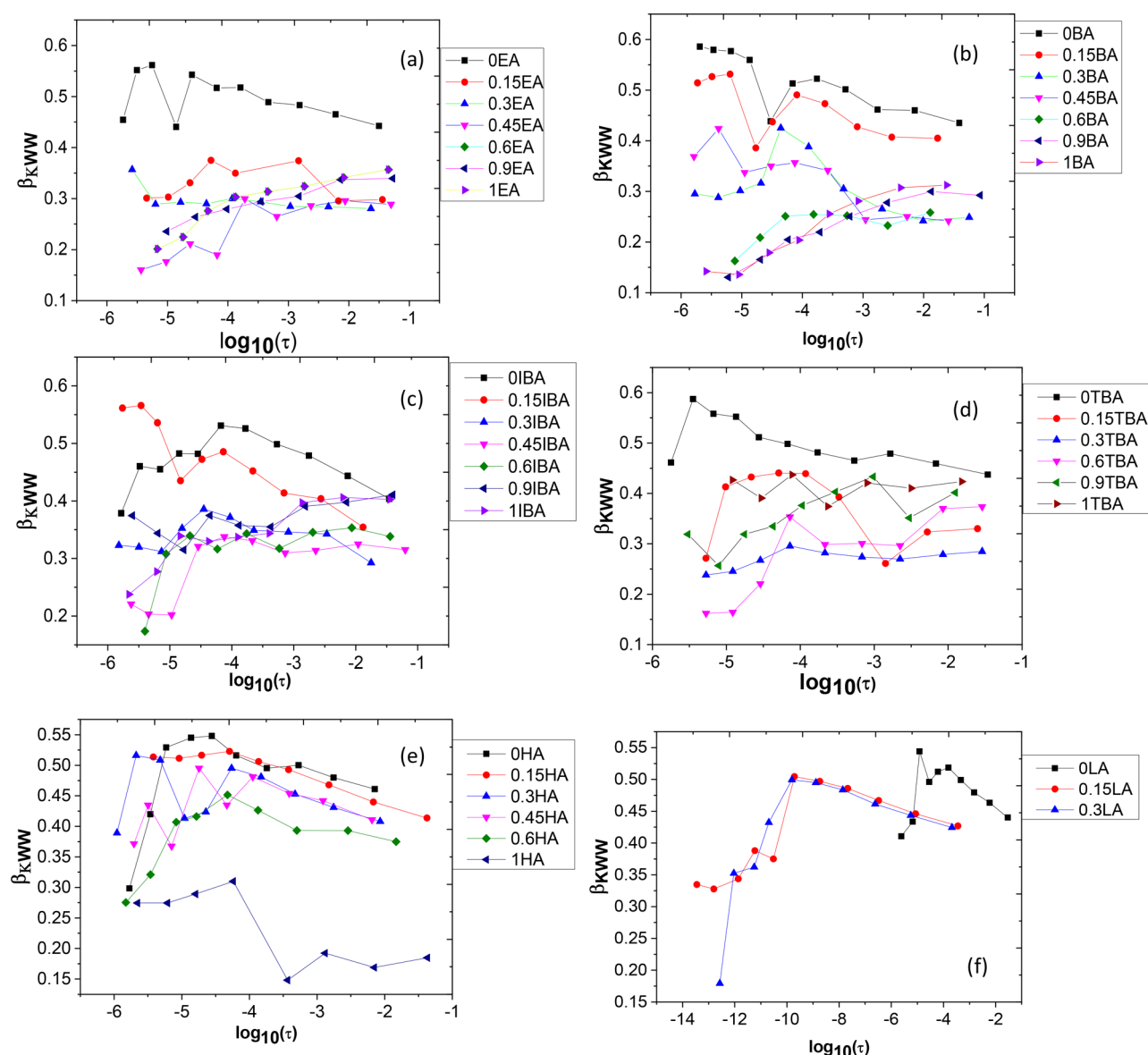


Figure 18. Values of β_{KWW} obtained from the Alvarez approximation plotted against $\log_{10} \tau$. The plots correspond to EHA-based statistical copolymer systems containing monomers of (a) EA, (b) BA, (c) TBA, (d) IBA, (e) HA, and (f) LA.

Figures 10 and 11 shows sample dielectric spectra from these copolymer systems as obtained from the HTBDS. Loss peaks with satisfactory signal to noise ratios allow further analysis of dynamic properties. The glass transition temperature (T_g) and fragility index (m) were calculated using the protocol described previously, with one exception. For several of the samples, we found that an excellent description of the loss peaks was provided by the Cole–Cole form, corresponding to fixing the shape parameter n in the HN function to 1.¹ In these cases, we therefore employed this form to fit. The resultant relaxation time–temperature data were fitted with the VFT model as described in the previous section. In all cases, coefficients of determination R^2 for the VFT fits were greater than 0.99, indicating that this form accounts for most of the variation in the relaxation time data. At high concentrations of LA, we were unable to detect relaxation processes beyond the signal to noise ratio of the instrument. It is likely that the long nonpolar side chains on LA simply result in insufficient dielectric response for measurement.

For each copolymer, T_g vs mass fraction data were compared to the Fox equation,⁵¹ an empirical formula for the glass transition temperatures of blends based on the pure component T_g values. Here, we used the pure component results from HTBDS measurements. In the case of HA and LA systems, where pure component data are missing, we obtained pure-component T_g values from the literature.^{52,53} As shown in Figures 12 and 13, trends in T_g with copolymerization are well-described by the Fox equation ($1/T_{g,blend} = \sum m_i/T_{g,i}$ with m_i the mass fraction of the i th component with glass transition temperature $T_{g,i}$). Our data indicate that, for these fairly weakly interacting polymers, the Fox equation holds not only for binary copolymers but also for ternary copolymers. In Figure 13, the values of experimental T_g are plotted against the mass fraction of EHA, with the exception of Figure 13g, where the concentration of EHA is 0. Each figure corresponds to a specific concentration of the third component. In polymer blends^{36–42} and some statistical copolymer systems⁵⁴ with high sequence length, localized concentration fluctuations result in the failure of the Fox prediction based on

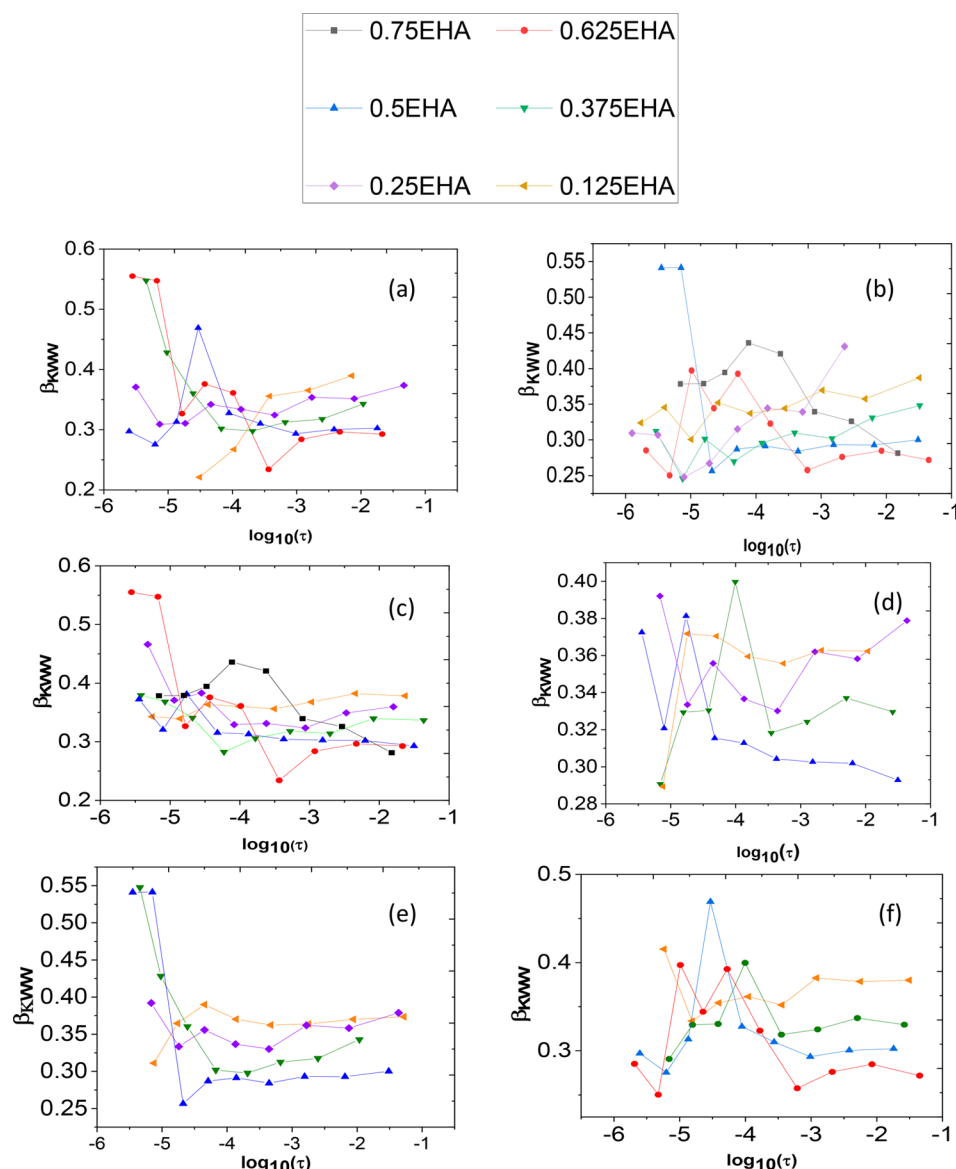


Figure 19. Values of β_{KWW} obtained from an Alvarez approximation plotted against $\log_{10} \tau$. The plots correspond to ternary copolymer systems containing (a) 0.125 IBA, (b) 0.25 IBA, (c) 0.375 IBA, (d) 0.125 EA, (e) 0.25 EA, and (f) 0.375 EA.

the bulk concentrations. In those cases, for the Fox equation to hold, the bulk concentrations have to be converted into effective concentrations based on the LM self-concentration model.^{36,37} In our binary and ternary copolymer systems, the RAFT copolymerization among these monomers possesses a reactivity ratio close to unity, and the resulting copolymers have relatively alternating backbones. Therefore, the localized concentration fluctuations of monomers can be neglected, such that the Fox equation holds.

As shown in Figures 14 and 15, the kinetic fragility index m based on an extrapolation of the data to 100 s does not exhibit an easily distinguished trend with composition. Because the fragility is a derivative quantity and is therefore more noise prone than T_g , we alternately obtained millisecond time scale fragilities m_{ms} by changing the value of the conventional time scale of T_g , denoted τ_g , to 0.001 s, as compiled in Figures 16 and 17. Because the data directly extend to the vicinity of 1 ms relaxation times, this eliminates the need for appreciable extrapolation and considerably improves the data quality. This alternate approach reveals an approximately clear dependence of fragility on

monomer composition. In most cases the relationship is approximately linear. We note that this is in contrast to blended mixtures, which tend to exhibit negative deviations from this mixing rule.⁵⁵ This raises the potential of tuning the breadth of the glass transition at constant T_g for a selected monomer pair via a combination of copolymerization and blending.

In several cases, notably EHA-EA and EHA-BA copolymers, there are pronounced deviations from a simple linear fragility mixing rule for the two copolymers. The case of EHA-EA, where the deviations from linear mixing are negative, is qualitatively consistent with work in blends.⁵⁵ These negative deviations can possibly be ascribed to a tendency for improvements in molecular packing in mixtures. The case of EHA-BA, which exhibits strong positive deviations from a linear mixing rule, is thus particularly interesting. Evidently, a combination of these monomers within the chain enhances fragility, potentially pointing toward a tendency toward poor molecular packing in this copolymer.

An additional property of interest in the dynamics of copolymers and other glass-forming liquids is the Kohlrausch–Williams–Watts (KWW) stretching exponent β_{KWW} . This

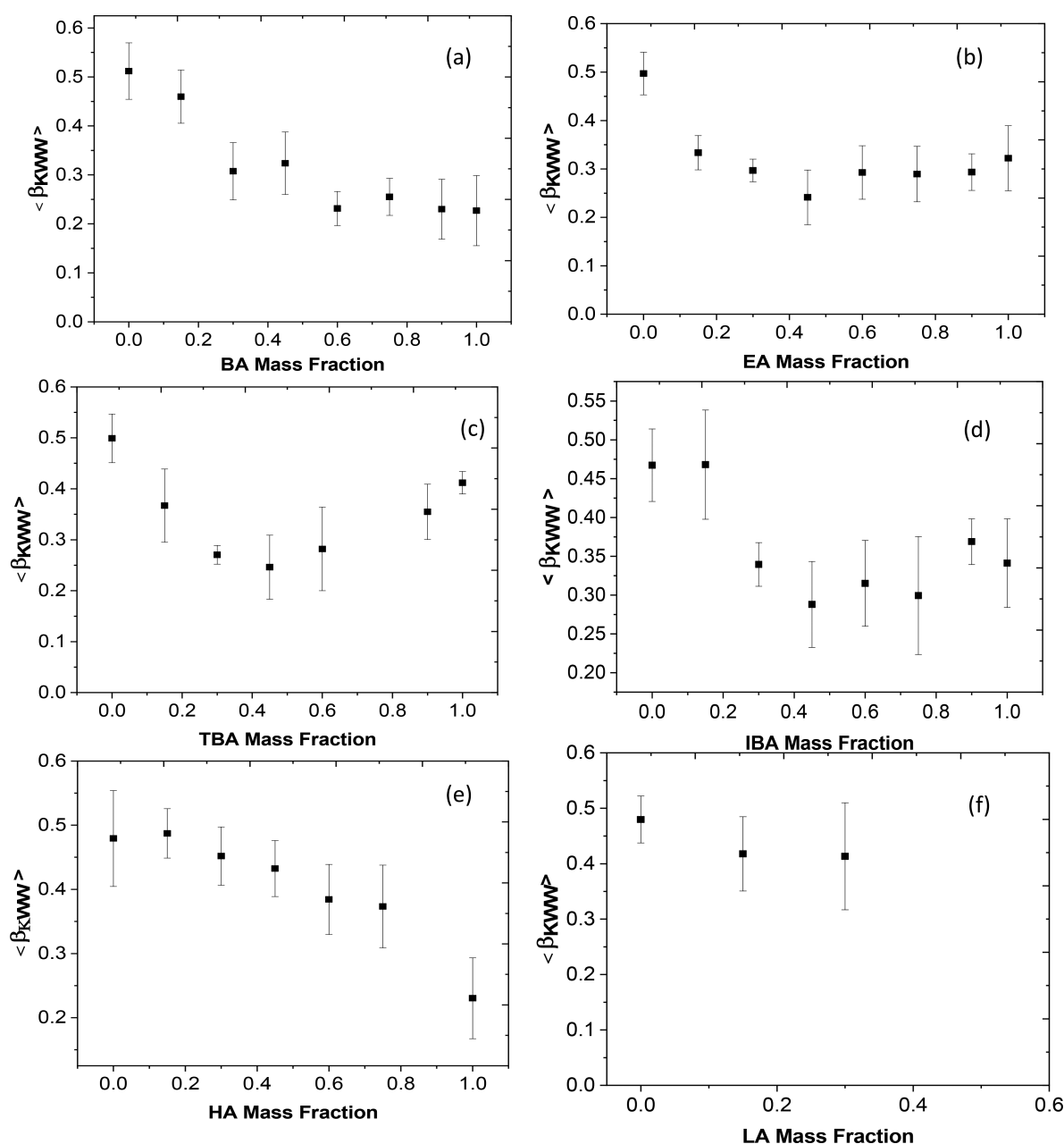


Figure 20. Values of β_{KWW} averaged over all temperatures. Error bars describe the magnitude of standard deviation. The plots correspond to EHA based statistical copolymer systems containing monomers of (a) BA, (b) EA, (c) TBA, (d) IBA, (e) HA, and (f) LA.

parameter is related to the breadth of the dielectric relaxation process. It is also commonly interpreted as a measure of the breadth of the underlying distribution of segmental mobilities. Alvarez et al.⁵⁶ have demonstrated an empirical correlation approximating time domain parameters with frequency domain parameters, wherein β_{KWW} can be approximated using the formula $\beta_{KWW} = mn$,^{1,23} where m and n are the HN shape parameters. We obtained values of β_{KWW} using this approximation, with values shown in Figures 18 (binary systems) and 19 (ternary systems). These results show that the stretching exponent varies with temperature. The typical thermal variation of β_{KWW} over the range of temperatures probed is roughly 0.2.

One feature of these data is uniform across all of the copolymer series—the limit of pure EHA exhibits the highest values of β_{KWW} . With decreasing EHA content, relaxation tends

to become more stretched. In order to examine trends in the stretching exponent as a function of monomer content, we average β_{KWW} over all temperatures measured for each system. These average β_{KWW} values are plotted vs mass fraction for each of the monomer pairs in Figures 20 (binary systems) and 21 (ternary systems), with error bars indicating the magnitude of thermal variation (measured as a temperature to temperature standard deviation) of β_{KWW} . The averaged results are consistent with β_{KWW} trends observed at individual temperatures. For binary systems, $\langle \beta_{KWW} \rangle$ values exhibit a decreasing trend with decreasing EHA content. For ternary systems, $\langle \beta_{KWW} \rangle$ fluctuates within the uncertainty range; this may suggest that the sheer number of distinct chemical moieties in the ternary copolymer leads to a substantial degree of dynamic heterogeneity and relaxational stretching, overwhelming specific composition effects.

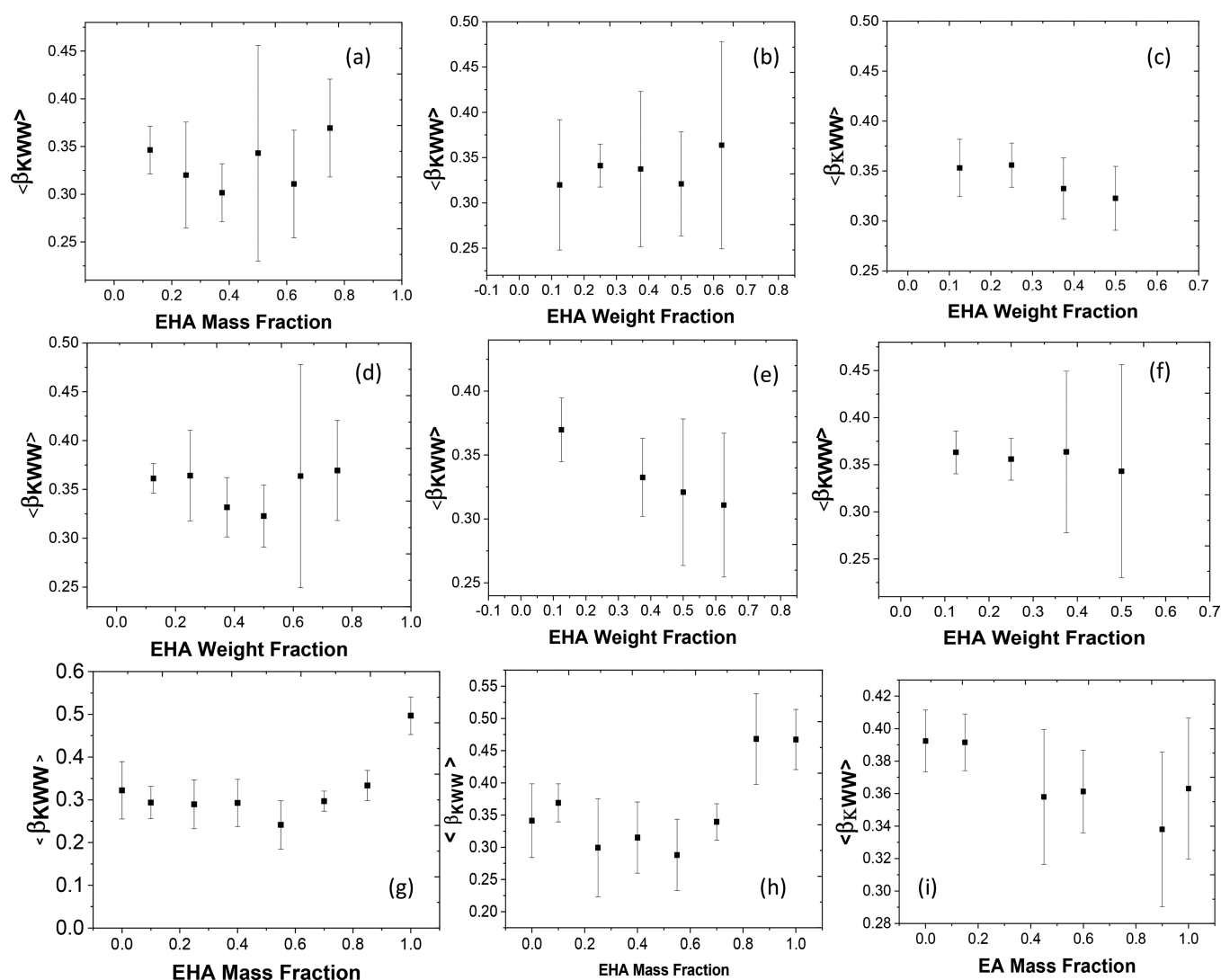


Figure 21. Values of β_{KWW} averaged over all temperatures. Error bars describe the magnitude of standard deviation. The plots correspond to ternary copolymer systems containing (a) 0.125 IBA, (b) 0.25 IBA, (c) 0.375 IBA, (d) 0.125 EA, (e) 0.25 EA, (f) 0.375 EA, (g) 0 IBA, (h) 0 EA, and (i) 0 EHA.

With these various dynamical properties determined, we now turn to the question of whether any universal correlations exist among them. First, we test for an anticipated linear relationship between m and T_g .⁵⁷ This relationship was proposed by Qin and McKenna, who showed that it follows from the classical Williams–Landel–Ferry equation⁵⁸ of dynamics in supercooled liquids. Moreover, they showed that distinct rough correlations of this kind appeared to hold for several classes of liquid. If this relationship is fundamentally true, one would expect to find such a correlation for the relatively chemically homogeneous group of polymers probed here.

As shown by Figures 22a,c, it is difficult to infer any relationship between m and T_g on the basis of values at an extrapolated 100 s time scale. In order to reduce the noise in these data, we thus return again to 1 ms values of m and T_g , which we denote as m_{ms} and T_{ms} , respectively. As shown by Figure 22b, the millisecond fragility of each type of binary copolymer exhibits a monotonic (and nearly linear) relationship with T_g as the mass fraction is varied. However, the strength of dependence of m on T_g (i.e., the slope in Figure 22b) varies strongly with monomer pair. Notably, there is little chemical diversity between these various copolymers; they do not, for example, introduce strong

interactions that have been argued to confound T_g/m correlations. The correlations for individual copolymer types in Figure 22b instead naturally emerge from the fact reported above that both T_g and m exhibit a monotonic dependence on composition for each monomer pair; with both relations being nearly linear. This naturally leads to a roughly linear correlation between T_g and m with varying composition for each monomer pair. Similarly, the terpolymer systems shown in Figure 22d vary the relative contents of EHA, IBA, and EA. As shown by Figure 22d, these systems happen to all fall on a single curve, and this is thus reflected in the ternary copolymers of these systems. However, it is clear from Figure 22b that this is coincidental and does not hold more broadly, and the striking deviations observed from any universal correlation between T_g and m in this fairly homogeneous system set speak strongly against any more general correlation between these properties.

Next, we test for the presence of any correlation between β_{KWW} and m . It has previously been argued, on the basis of the Coupling Model of glass formation, that these two quantities are strongly correlated.²⁸ Here, we test for such a relationship either employing the temperature-averaged values of β_{KWW} described above or using a 1 ms value of β_{KWW} determined by interpolation

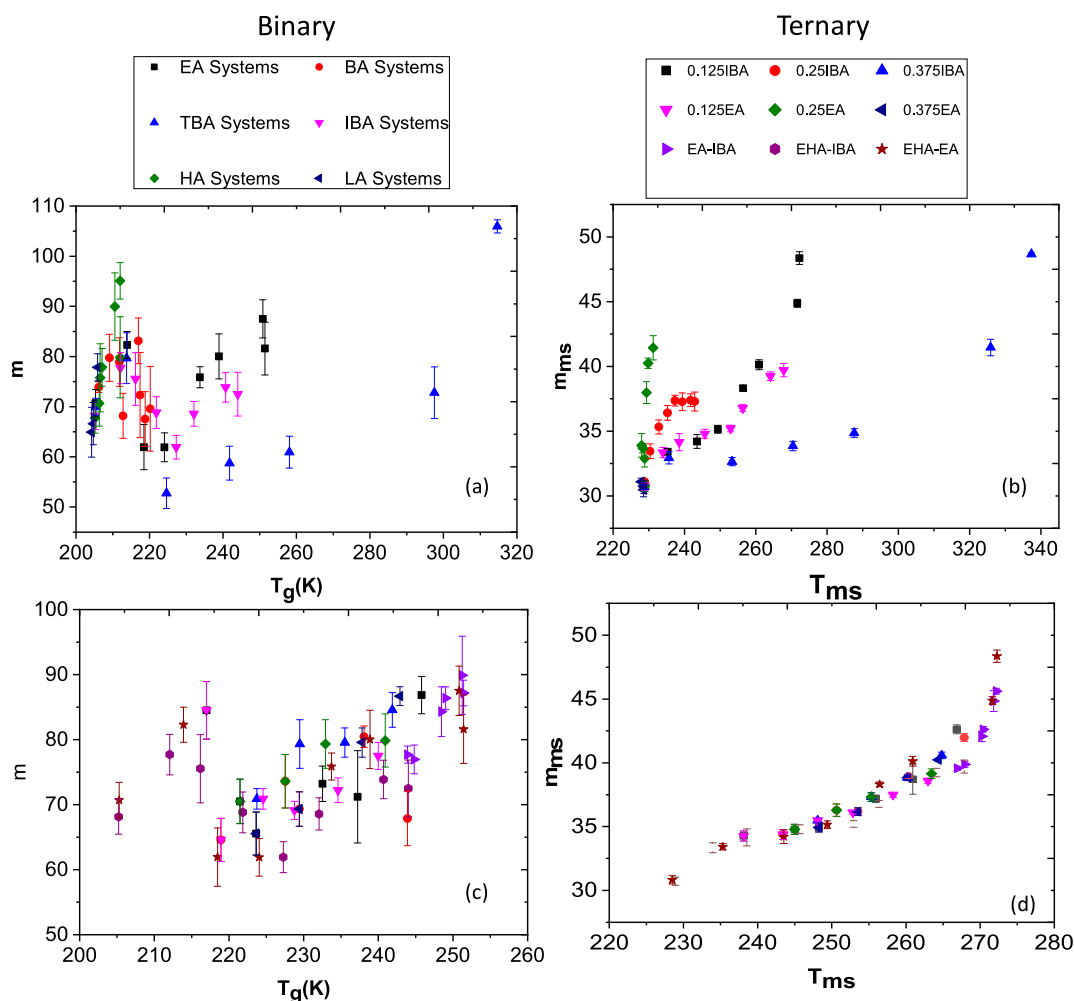


Figure 22. Relationships between T_g and m . (a) m vs T_g for binary systems, with both computed at 100 s. (b) m_{ms} plotted vs T_{ms} (i.e. m and T_g computed at 1 ms) for binary systems. (c) m vs T_g for ternary systems, with both computed at 100 s. (d) m_{ms} plotted vs T_{ms} (i.e. m and T_g computed at 1 ms) for ternary systems. Error bars are standard errors for m as a VFT fit parameter to each relaxation time data set. T_{ms} is in units of Kelvin.

of the temperature-dependence β_{KWW} data. As shown by Figure 23 for both the binary and ternary copolymer systems, these data exhibit no appreciable correlation between β_{KWW} and m via any of these approaches. Of particular interest are Figure 23b and Figure 23d, where β_{KWW} and m are compared in a completely consistent way, with both determined at 1 ms. The data suggest that these quantities are uncorrelated—i.e., the fragility of glass formation in no way predicts the extent of dielectric stretching or vice versa. This is consistent with arguments of Dyre to this effect.⁵⁹

Finally, we examined the relationship between β_{KWW} and T_g . To our knowledge, there has been no prior suggestion of a general correlation between these quantities. As shown by Figure 24a,b, the temperature-averaged stretching exponent $\langle\beta_{KWW}\rangle$ exhibits an appreciable correlation with 100 s glass transition temperatures, with an initial negative correlation followed by a weak upturn for T_g values greater than 230 K. If we instead consider both values determined at 1 ms (Figure 24c,d), a similar relationship is observed. In both cases, the data suggest a non-monotonic dependence of β_{KWW} on T_g , with a minimal value of β_{KWW} when T_g is near 230 K, with β_{KWW} growing linearly as T_g deviates either to the negative or positive side of this value. A natural question is whether this trend simply reflects the EHA fraction of each copolymer, since the homopolymer limit of

β_{KWW} is considerably higher for EHA than for any of the other monomers here, and EHA also possesses the limiting minimum homopolymer T_g . However, when we plot β_{KWW} vs EHA content in Figure 24e,f, the correlation between stretching and EHA content is found to be relatively weak; the decreasing and increasing trendlines in Figures 24a–d have R^2 values greater than 0.5. Evidently simple control by EHA content is not the origin of the observed correlation between T_g and stretching.

DISCUSSION AND CONCLUSIONS

We report on a new strategy enabling high-throughput broadband dielectric spectroscopy (HTBDS). HTBDS parallelizes thermal equilibration time, which dominates isothermal, equilibrium BDS measurement times, across 48 samples. As a consequence, it realizes an order of magnitude improvement in the throughput of this technique. This advance is enabled by a parallel sample stage and coaxial switching system enabling automated measurement of multiple samples within the same environmental chamber. A comparison of results for commercially available polymers obtained via this instrument shows good agreement with measurements on a commercially available sample stage, validating the high-throughput broadband dielectric spectrometer. We note that BDS measurements

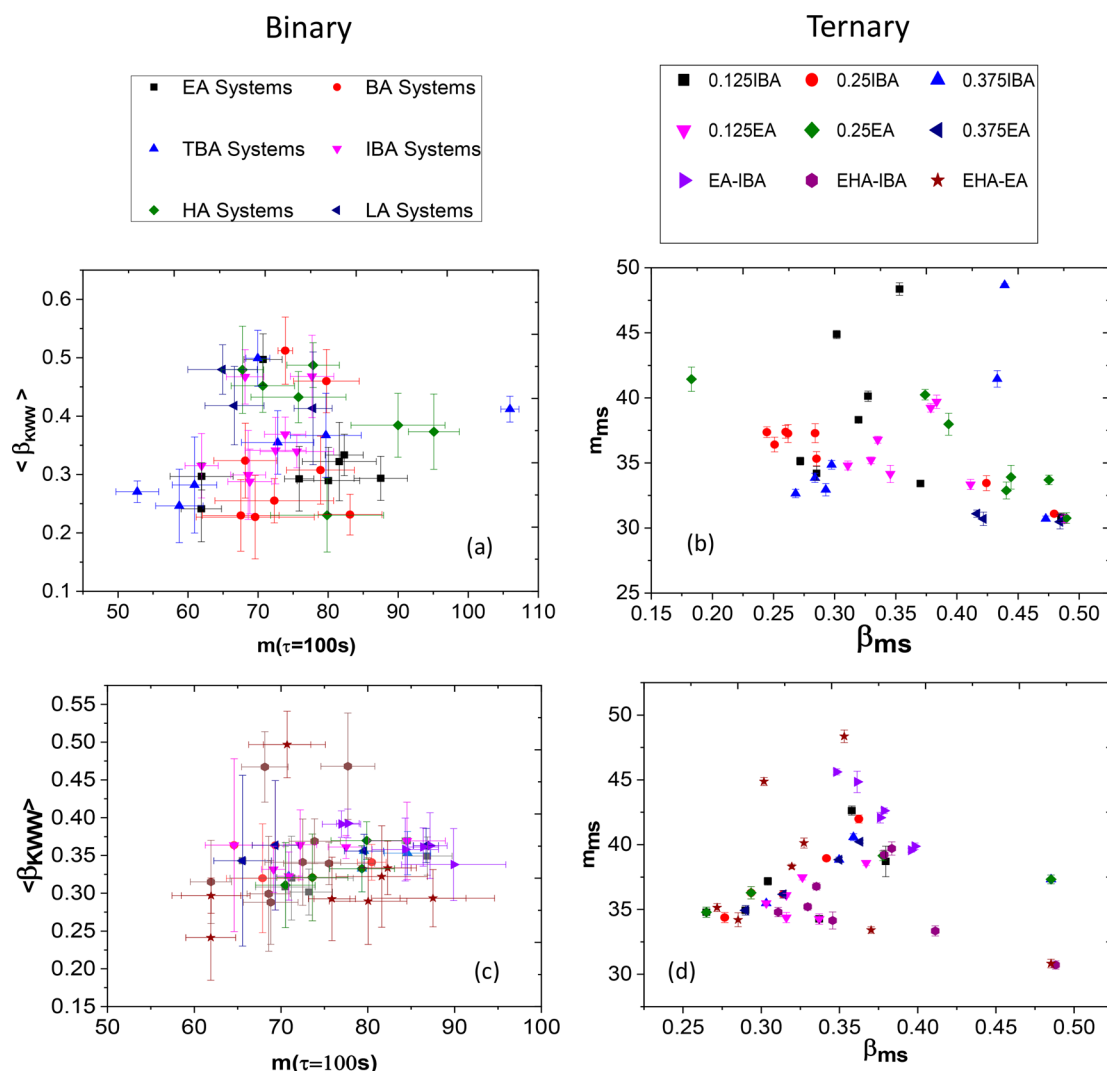


Figure 23. (a) $\langle \beta_{KWW} \rangle$ vs m at 100 s for binary systems. (b) m_{ms} vs β_{ms} for binary systems. (c) $\langle \beta_{KWW} \rangle$ vs m at 100s for ternary systems. (d) m_{ms} vs β_{ms} for ternary systems. Error bars on m are standard errors for m as a VFT fit parameter to each relaxation time data set. Error bars on $\langle \beta_{KWW} \rangle$ quantify the standard deviation of β_{KWW} over the range of temperatures probed.

are often made either with short equilibration times (where the sample cell can still be reaching thermal equilibrium during the measurement process) or by isochronal measurements (where the temperature is scanned at a fixed heating/cooling rate and measurements are made at a single frequency) that can make single sample measurements far quicker than those of our single sample cryostat measurements; however, these measurements create uncertainties, particularly at lower frequencies,⁶⁰ that can induce larger uncertainties in the extrapolation to a relaxation time of 100 s and so should be avoided whenever possible. The present approach is therefore focused on isothermal, equilibrium measurements where these issues are not present.

We employ this capability to probe glass formation and dynamics in binary and ternary acrylate copolymers synthesized in parallel via RAFT polymerization in a solvent-handling robot. Results for T_g are consistent with the Fox glass transition mixing rule. We find that fragilities of glass formation, when they are determined at 1 ms without extrapolation, exhibit in most cases a roughly linear dependence on monomer concentration, consistent with a simple averaging rule of fragility on mixing. We do observe two cases with appreciable deviations from linearity, with one case exhibiting positive deviations and the other

negative. These results are in contrast to prior work pointing to consistently negative deviations from fragility averaging on blending, as opposed to copolymerization.⁵⁵

Finally, we employ the data accumulated for these systems to test several proposed correlations between these distinct dynamical properties. The results indicate that there is no general correlation between glass transition temperature and fragility for these glass formers, in contrast to prior expectations. Given that these copolymers are relatively chemically homogeneous and lack strong interactions that might be expected to complicate correlations of this sort, these findings speak rather strongly against any fundamental correlation between T_g and fragility. Similarly, we find no general correlation between fragility and the degree of dielectric stretching, again in contrast to prior expectations. Instead, we find that dielectric stretching is correlated with T_g in this set of systems, with a tendency toward decreasing stretching with a decrease in T_g below approximately 230 K. Additional study with a more chemically diverse data set will be needed to determine whether this correlation can be generalized beyond these acrylate copolymers.

While the particular HTBDS design reported here targets 48 solid samples, this approach can be easily extended to other

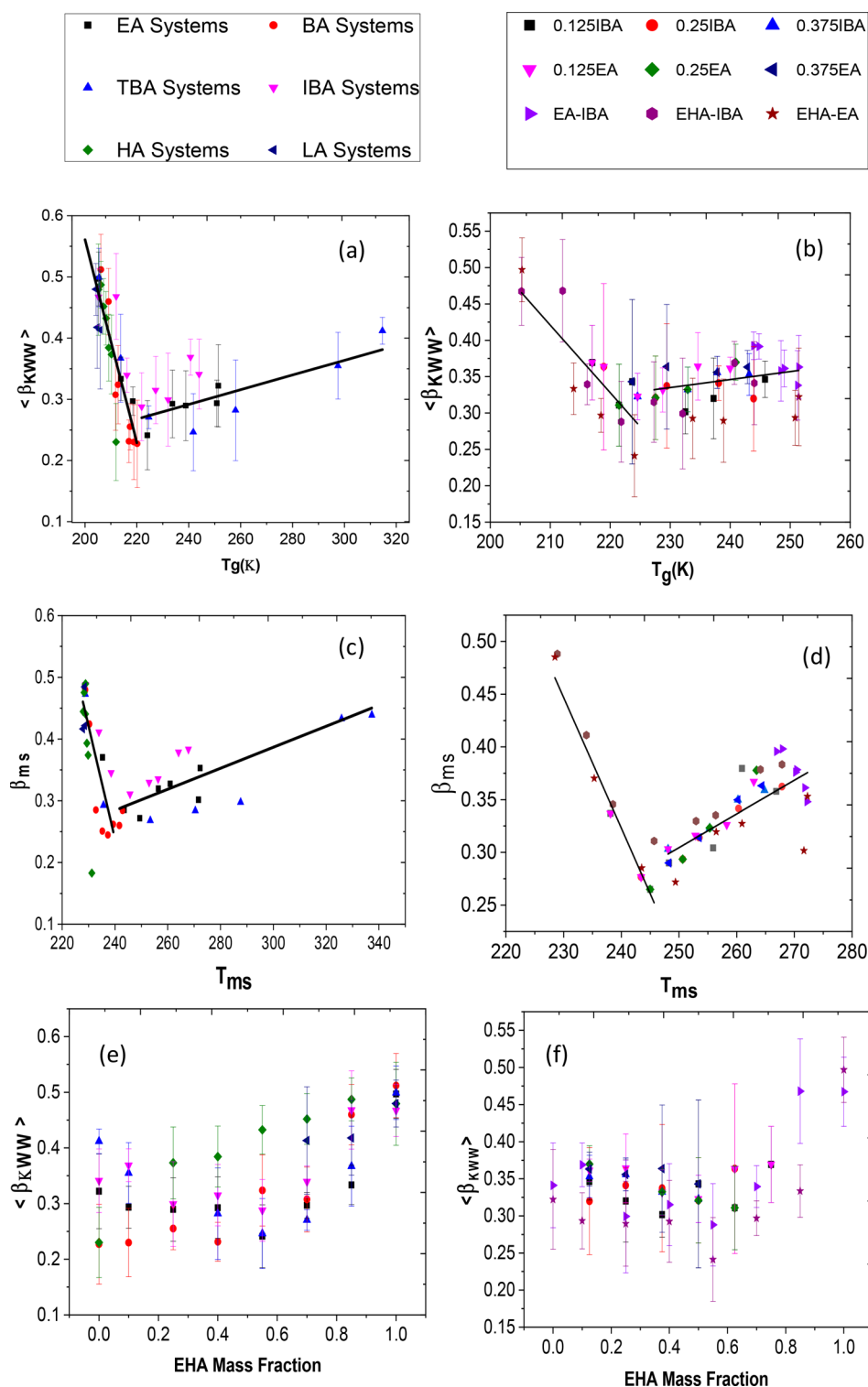


Figure 24. (a) $\langle \beta_{KWW} \rangle$ vs T_g for binary systems. (b) β_{ms} vs T_{ms} for binary systems. (c) $\langle \beta_{KWW} \rangle$ vs EHA composition for binary systems. (d) $\langle \beta_{KWW} \rangle$ vs T_g for ternary systems. (e) β_{ms} vs T_{ms} for ternary systems. (f) $\langle \beta_{KWW} \rangle$ vs EHA mass fraction for ternary systems. Error bars on $\langle \beta_{KWW} \rangle$ quantify the standard deviation of β_{KWW} over the range of temperatures probed.

numbers of samples simply by altering the number of coaxial switches and sample sites. Extension to measurement of liquid samples would likewise require a modest alteration of the parallel-plate capacitor geometry. A comparison of measurements on three polymer samples via HTBDS to measurements on a commercially available testbed indicate that the data quality is comparable and the results are highly reproducible.

In particular, segmental relaxation times, glass transition temperatures, and kinetic fragilities obtained via the high-throughput approach agree with those obtained via a commercially available sample stage. Given the central importance of these quantities to the performance properties of polymers and other soft materials, a well-validated capacity for their high-throughput determination raises new opportunities for high-throughput materials

design in this area. Beyond these properties, BDS also provides access to a range of other properties of technological interest. For example, the ability to perform high-throughput screening of ion conductivity has the potential to accelerate design of new ion-conducting media for next-generation energy storage applications.⁶¹

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscombsci.8b00160.

Additional NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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