

PROTON NMR CHARACTERIZATION OF ROOM-TEMPERATURE AGING IN ISOTACTIC POLYPROPYLENE AND ETHYLENE/OCTENE COPOLYMERS

D.L. VanderHart¹, C.R. Snyder¹, and R.G. Alamo²

¹Polymers Division, NIST
Gaithersburg, MD 20899-8544

²Department of Chemical Engineering
FAMU/FSU
Tallahassee, FL 32310

Introduction

In this paper, we utilize the relatively high sensitivity of proton NMR to revisit a well recognized (1) problem of ambient-temperature aging in 2 semicrystalline polymers whose non-crystalline (NC) regions have glass transition temperatures, T_g , substantially lower than ambient. The exact mechanism of aging above T_g is still in dispute (2). One would not expect aging above T_g ; however, the existence of crystalline (CR) regions creates the expectation that topologically, not all NC repeat units will be equally mobile. There might also be opportunity for rearrangements into stable, 'crystal-like' structures. Here we use NMR to study aging in the hopes of gaining greater insight into the aging process. We do not claim that NMR is a good way to do routine aging studies since the spectrometer is tied up inefficiently for rather long periods; however, we show that NMR has excellent sensitivity for detecting changes in mobility associated with aging. NMR also offers the possibility of a more detailed insight into the aging process.

We did not initially set out to study aging. Rather, it was after a drying cycle at 89 °C in a Si-filled isotactic polypropylene (iPP) nanocomposite that we stumbled on these lineshape changes and then found them also associated with the corresponding unfilled iPP, designated iPP-1. Since iPP-1 was not very thoroughly characterized, a second, well characterized iPP-2 sample was studied to ascertain whether a reduction in defect content, polydispersity and amorphous fraction would modify the extent of aging. Melt temperatures for iPP lie ≈ 70 °C above the thermal initiation temperatures used herein. In contrast, the ethylene/octene (EO) copolymers were examined after rather rapid melt crystallization in order to couple more closely with existing studies (2,3).

Experimental

Samples. iPP-1 is a commercial Ziegler-Natta-catalyzed iPP, marketed under the name Pro-fax 6523 (4) and manufactured by Basell; iPP-2 is a non-commercial metallocene-catalyzed sample (mass-averaged relative molecular mass, M_w , of 200,500 g/mol, a polydispersity, PD, of 2, and a defect content of 0.41 mole fraction of 2,1 regio erythro defects) which had been used in a previous study (5). Lacking available molecular-mass information about iPP-1, we did gel permeation chromatography (GPC) on both iPP-1 and iPP-2, for comparative purposes, obtaining the following values for iPP-2: $M_w = (1.7 \pm 0.1)$ times that of iPP-1 and $PD = 4.5 \pm 0.5$. Stereo-defect content of iPP-1 was estimated from solid state ¹³C results (6) as (1.6 ± 0.5) mole fraction.

EO-15 ($M_w = 98,000$, $PD = 2.15$) and EO-9 ($M_w = 120,000$, $PD = 2.03$) are designations for metallocene-catalyzed ethylene/octene random copolymers which respectively contain (14.8 and 9.0) mole fraction octene.

Thermal treatments. iPP samples were originally melt crystallized by cooling at 1°C/min from the melt at 195 °C. Aging times, t_{age} , were initiated when iPP samples were removed from the temperature bath which was at or below 89 °C. For the EO samples, $t_{age} = 0$ is the time of melt-removal from a 100 °C bath. All samples were cooled rather quickly in air.

NMR. All proton NMR experiments were conducted at 7.05 T (300 MHz) and at (20 °C \pm 1.5 °C) on a Bruker Avance spectrometer (Bruker Instruments, Inc. of Billerica, MA) equipped with a magic-angle-spinning, (MAS) low-background-signal probe built by Doty Scientific, Inc. of Columbia, South Carolina. Mainly Bloch-decay signals were observed at a MAS frequency of (2500 \pm 20) Hz. Temperature was not controlled owing to adequate temperature control in the room. Pressures used for spinning were very modest, and cause departures from ambient temperatures less than 2 °C. Within any single aging experiment, temperatures were constant as a result of the sample remaining in the probe. Radiofrequency field strength corresponded to a nutation frequency of 167 kHz (1.5 μ s 90° pulse).

Aging was monitored using equilibrium, (M_0) Bloch-decay spectra [24 scans, 5 s delay time, total collection time of 2 min, 2.5 μ s receiver dead time, 1 μ s dwell time, 65536 data points for both free-induction-decays and Fourier-transformed (FT) spectra, 10 MHz analog filter widths on the receiver/digitizer so that bandwidth was effectively determined by the probe]. In obtaining the FT spectra, only a zero-order phase correction was applied. Since our data analysis features the presentation of difference spectra, it is important that the parent spectra giving rise to these differences are uniform in dc-offset, gain and phase. Careful baseline adjustments, careful phase corrections, and careful rescaling of spectra to both compensate for drifts in gain and maintain constant total integrals were all important aspects of data analysis. Thus, difference spectra with null total integrals are generated.

At convenient times between the samplings of the M_0 spectra, quick assays of the proton longitudinal relaxation time, T_1^H , were also made. The (180°- τ - 90°-observe-T) inversion-recovery sequence (7) was used after calibrating the 180° pulse for each measurement. The "zero-crossing" time, τ_{null} was measured and assumed proportional to the longitudinal proton relaxation time, T_1^H , (for a single-exponential decay, $\tau_{null} = T_1^H/\ln 2$). Since T_1^H is sensitive to molecular motions in the vicinity of the Larmor frequency near 2×10^9 rad/s, aging processes that either reduce the number of non-crystalline chains or constrain them in a way that affects the amplitude and/or frequency of these fast motions can create a change in T_1^H . While rotating methyl groups in both the CR and NC regions provide much of the motion in this frequency range, the NC methine and methylene protons also provide strong contributions to T_1^H . A significant change in the fraction of NC chains or their angular amplitudes of motion, should yield a measurable change in T_1^H . Early on we realized that paramagnetic oxygen can cause as much as a 6% change in T_1^H ; hence, all thermal treatments, after the first, were in air.

Finally, we also carried out a few multiple-pulse (8) (MP) experiments, intended to examine issues of motional modification and crystallinity change. The MP aspects of these experiments centered around the idea of *relaxation under MP*. Using the MREV-8 MP sequence (8) and with the proper prepulse and receiver phase, one can observe so-called T_{1xz} relaxation (9) which is a) primarily sensitive to motions in the mid-kHz regime and b) uncomplicated by spin diffusion (10) with neighboring protons. Low mobility of the backbone protons and higher-frequency rotation of methyl groups in the CR region combine to give long- T_{1xz} character to all CR protons in these iPP's. We adopted a definition (11) of crystallinity in iPP based on the relative strength of the longest-relaxing ($T_{1xz} \approx 150$ ms) component. Static samples were used for these T_{1xz} experiments to avoid artifacts not related to molecular motion. MP experiments were not very useful for the EO samples; the longest- T_{1xz} component arises, in part, from NC protons having very high mobility.

Results and Discussion

iPP. In Figure 1, two experimental Bloch-decay spectra are shown for iPP-1 at different aging times following heat treatment in vacuum at (85 \pm 5) °C for 2 d. The earliest analysis time was 6 min (1A); also shown is the spectrum (1B) at $t_{age} = 5740$ min \approx 4 d. Spectra 1C through 1H are zero-integral difference spectra reflecting spectral changes associated with aging; the aging times involved in the differences are given. Positive-going features of the difference spectra represent intensity lost upon aging; negative intensity is that gained. Several observations, based on Figure 1, may be made. First, the negative-going intensities in the difference spectra have widths indistinguishable from the widest components of 1A or 1B; hence, the changes could be considered as crystallization, provided that the broadest lineshape components all arise from the CR regions. Second, the relative intensity of the broad negative features of the difference spectrum, 1G, correspond to a 2.3 % increase in crystallinity. Third, the zero-integral difference spectra show the same lineshape over the 4 d of aging, no matter what pairs of aging times are involved (illustrated in the bottom spectrum of Figure 1); this observation is not expected if aging involves a gradual restriction of motion for all NC chains. Fourth, the intensities in 1C to 1G grow linearly in $\log(t_{age})$ as illustrated in Figure 2. We note also that the changes in T_1^H accompanying the 4 d of aging are negligible (<0.5 % change), provided the heating that initiates aging takes place in air rather than a vacuum (O_2 retention). This is surprising since aging has reduced the amount of NC material by 7 % to 9 % and since relaxation of the CR is significantly influenced by NC relaxation. A possible implication is that the structures

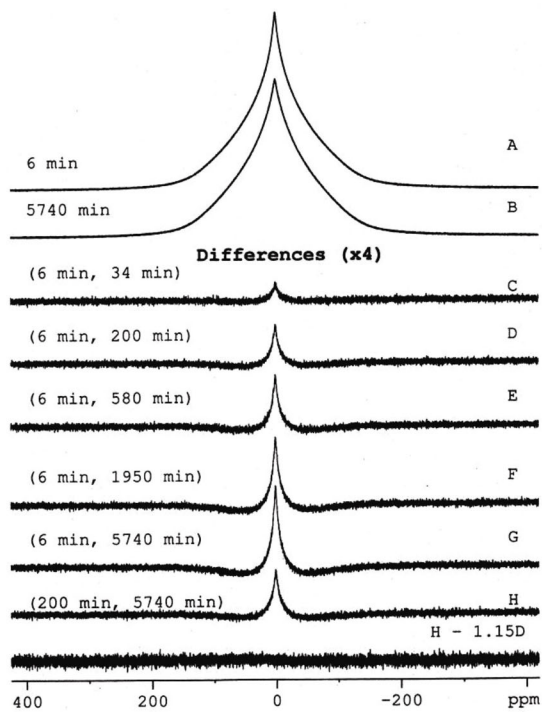


Figure 1. 300 MHz proton spectra of iPP-1 as a function of aging time after an 85 °C exposure for 2d. Spectra are both experimental (A,B) and zero-integral difference spectra (C-H). Associated aging times, or pairs of aging times are given. The bottom spectrum illustrates that in the difference spectra, only intensities change; lineshapes do not evolve over this 4d aging period.

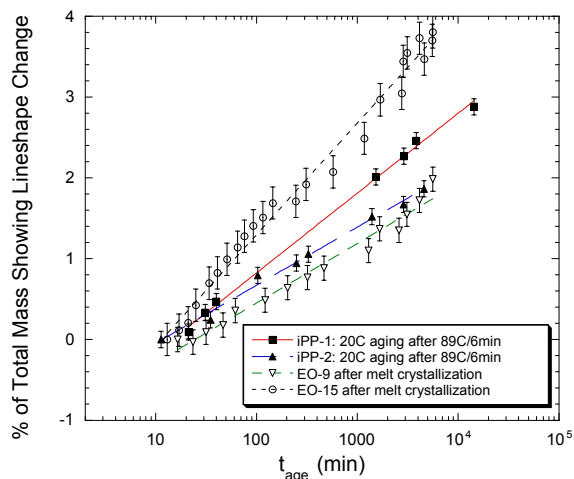


Figure 2. Minimum fractions whose mobility is altered by the aging process, versus aging time. Uncertainties shown are one standard deviation. EO data have more uncertainty, reflecting the fact that the EO lineshapes, relative to those of iPP, are more temperature sensitive at the observation temperature.

formed by aging are isolated from each other on a distance scale considerably larger than the long spacing. Behavior of iPP-2 was similar to iPP-1 except for a 30 % reduction in amount (**Figure 2**). Also, all aged structures are destroyed by reheating to the temperature of the original thermal treatment; this precludes aging as increasing the thickness of the primary crystallites. **EO.** The ethylene/octane copolymers are distinct from the iPP samples in that the high fractions of hexyl branches, assumed to be excluded from the CR regions, make the NC fraction dominant and the opportunity for crystallization, either primary or secondary, strongly dependent (2) on copolymer sequence, assumed random. At ambient temperature, there is a lot of molecular mobility in the NC regions of these polymers; moreover, “crystallinity” is an ill-defined concept, owing, for example, to the fact that in EO-15, the least mobile structures, from a proton lineshape point of view, all are characterized by substantial mid-MHz and mid-kHz spectral densities, as judged by $T_{1\rho}$ values less than 3 ms and ^{13}C $T_{1\rho}$ values of less than 400 ms at 25 MHz. So, if CR structures exist, they incorporate substantial, higher-frequency motions. We only note that the lineshapes change as a signature of aging, but we do not postulate crystallization as the dominant process as we did in the iPP case. The relationship of our observations to differential scanning calorimetry data taken on similar materials (2,3) will be discussed.

Interpretation of the difference spectra, cited herein as a measure of aging, requires a few more comments. In **Figure 2** we interpret these spectra in terms of a fraction of material that is changing mobility with t_{age} . It is certainly more accurate to say that the fractions deduced in this way are *minimum* fractions which, in our examples, correspond to *large* changes in mobility. In fact, the only case where we can confidently say that this fraction is the true fraction is the case where the lineshape consists of only 2 components of different lineshape. In the extreme contrasting case where there is a continuum of lineshape components, it is, in principle, possible that a large number of NC protons could each become a little less mobile with t_{age} so that, even though many protons are slightly affected, the only population which would *appear* to be depleted is, consistent with our observations, the most mobile population. Hence, in terms of distinguishing between the mechanisms (2) of secondary crystallization and entropic loss in NC regions, we would like to know more about the *localization* of the populations whose mobilities are changing. For the iPP samples, the constant *shape* of all difference spectra and the constancy of $T_{1\rho}$ with t_{age} both suggest, but do not prove, a more localized picture of the mobility modifications.

Conclusions

Using Bloch-decay difference spectra, lineshape changes upon aging can be followed with excellent sensitivity for semicrystalline polymers whose T_g lies below the temperature of analysis. Auxiliary NMR experiments involving relaxation in both the laboratory and toggling frames can be used to further evaluate the lineshape changes in terms of crystallization and the localization of the regions of mobility modification.

References

- (1) Struik, L. C. E. *Plastics Rub. Proc. Appl.* **1982**, *2*, 41-50.
- (2) Alizadeh, A.; Richardson, L.; Xu, J.; McCartney, S.; Marand, H.; Cheung, Y. W.; Chum, S. *Macromolecules* **1999**, *32*, 6221-6235.
- (3) Carrilero-Borbujo, I., Private communication of unpublished master's thesis, FAMU-FSU College of Engineering, 2002.
- (4) Certain commercial companies are named in order to specify adequately the experimental procedure. This is no way implies endorsement or recommendation by the authors or their agencies.
- (5) Vanderhart, D.L. Nyden, M.R., Alamo, M.-H. Kim, R.G., Mandelkern, L. *Macromolecules* **2000**, *33*, 6078-6093.
- (6) Vanderhart, D.L. Nyden, M.R., Alamo, M.-H. Kim, R.G., Mandelkern, L. *Macromolecules* **2000**, *33*, 6078-6093.
- (7) Farrar, T.C., Becker, E.D. *APulse and Fourier Transform NMR*, Academic Press, 1971, p. 20-21.
- (8) Rhim, W.-K.; Elleman, D.D.; Vaughan, R.W., *J. Chem. Phys.* **1973**, *59*, 3740.
- (9) Vega, A.J.; Vaughan, R.W., *J. Chem. Phys.*, **1978**, *68*, 1958.
- (10) “*The Principles of Nuclear Magnetism*”, Abragam, A., Oxford University Press, **1961**, Chap. V.
- (11) Havens, J.; VanderHart, D.L., *Macromolecules* **1985**, *18*, 1663-1676.