

Blends of Fatty-Acid-Modified Dendrimers with Polyolefins

BARRY J. BAUER,¹ AISSA RAMZI,² DA-WEI LIU,¹ ROLF L. SCHERREBERG,² PETER FROEHLING,² JACQUES JOOSTEN²

¹ National Institute of Standards and Technology, Polymers Division, Building 224, Room 314, Route 270 and Quince Orchard Road, Mailstop 8542, Gaithersburg, Maryland 20899

² DSM Research, P.O. Box 18, NL-6160 MD, Geleen, The Netherlands

Received 11 January 1999; revised 8 September 1999; accepted 20 September 1999

ABSTRACT: Blends were made by solution and melt-mixing fatty-acid-modified dendrimers with various polyolefins. Small-angle neutron scattering (SANS) was used to determine the miscibility of the blends. Poly(propylene imine) (PPI) dendrimers G1, G3, and G5 [DAB-*dendr*-(NH₂)_y] with $y = 4, 16,$ and $64,$ were reacted with stearic acid or stearic acid-*d*₃₅ forming amide bonds. The modified dendrimers were then blended with high-density polyethylene (HDPE), high-density polyethylene-*d*₄ (HDPE-*d*₄), low-density polyethylene (LDPE), amorphous polypropylene (PP), or an ethylene-butylene copolymer (E-co-B). Limiting power law behavior shows that all of the blends are immiscible. It is likely that the dendrimers form a second phase, being finely dispersed, but thermodynamically immiscible. © 2000 John Wiley & Sons, Inc.* J Polym Sci B: Polym Phys 38: 95–100, 2000

Keywords: dendrimer; fatty acid; SANS; phase separation

INTRODUCTION

Dendrimers are a relatively new class of macromolecules constructed with highly regular branching, having tree-like structures that emanate from a central core.^{1–6} The structure of these three-dimensional polymers allows control of their size, shape, molecular weight, topology, and surface chemistry to an extent unprecedented in polymer science.^{7,8}

Dendrimers have been shown to have a uniform spherical shape in solution that resembles the structure of a micelle.⁹ Incorporation of small molecules in the dendrimer has been demonstrated by the “dendritic box” in which dye molecules are trapped within the dendrimer.^{10,11} The fact that a dendrimer has the shape of a spherical

micelle, but is a covalently bonded, stable structure, suggests that it may be a powerful tool in dispersing molecules in a solution or polymer blend.

Recently, dendrimers have been modified by attaching hydrophobic groups to the terminal units of dendrimers.^{12,13} This further accentuates the micellar nature of the dendrimers. Hydrophobic dendrimers such as polyethyleneimine dendrimers (Astramol™)^{4,14} can be reacted with stearic acid resulting in amide bonds between the dendrimer and the hydrophobic stearic acid groups. The solubility characteristics are changed dramatically, with the dendrimers becoming soluble in hydrocarbon solvents. The interfacial and self-assembly properties of fatty-acid-modified dendrimers have recently been described.¹⁵

From recent work it appears that the combination of fatty-acid-modified dendrimers (FADs) with polyolefins leads to interesting new applications. It turns out that FADs can stabilize the dispersion of polar dye molecules in apolar polyolefins such as polyethylene,¹⁶ by complexing the

Correspondence to: B. J. Bauer (E-mail: barry.bauer@nist.gov)

Journal of Polymer Science: Part B: Polymer Physics, Vol. 38, 95–100 (2000)
© 2000 John Wiley & Sons, Inc. *This article is a US Government work and, as such, is in the public domain in the United States of America.

dye molecules as guests into the modified dendrimer, followed by blending the dendrimer–dye complex into the polymer matrix. Another application, which makes use of FADs, is a dendrimer-modified polypropylene (PP) fiber.¹⁷ This is obtained by blending a small quantity of FAD with PP, followed by spinning. The resulting dendrimer-containing fibers can be dyed by aqueous solutions or dispersions of conventional dyes.

The nature of the dispersion of the FADs in the polyolefins in these applications is not known. One possibility is that the dendrimers are molecularly dispersed in the polymeric matrix. Another possibility is that the dendrimers form a second phase, being finely dispersed, but thermodynamically immiscible.

Small-angle neutron scattering (SANS) has been used routinely to determine the miscibility of polymer blends.^{18,19} First, it can easily distinguish miscible and immiscible blends, most easily from the power law behavior at a high scattering angle. In miscible cases, where the polymer molecules are molecularly dispersed, the size, shape, and interaction parameter of the components can be measured. In immiscible blends, phase size and interfacial width can be extracted.

EXPERIMENTAL

Materials

In order to gather this information from a SANS experiment, it is necessary that sufficient neutron contrast exists. This is most commonly achieved by deuterium labeling of one of the components. In this study, three generations G1, G3, and G5 of poly(propylene imine) dendrimers (Astramol™),^{4,14} with $y = 4, 16,$ and 64 primary amine groups [DAB-*dendr*-(NH₂)_{*y*}], were modified with fatty acid (Octadecanoic, C₁₈). The modification consisted of the conversion of the primary amine groups into amides.^{12,13} In this case, about 2.5 mmol of fatty acid, hydrogenous or deuterated, was added to an equivalent amount of poly(propylene imine) dendrimer and 20 mL of xylene. The mixture was heated to 160 °C while stirring under a slow stream of nitrogen in a two-necked flask, with a gas inlet and a Dean–Stark trap. After 1 h of reaction at 160 °C all xylene was distilled off carefully, and the product was allowed to cool to room temperature. The dendrimer modified with octadecanoic acid-*d*₃₅ is

designated dendrimer-*d* and with octadecanoic acid-*h*₃₅ is designated dendrimer-*h*.

HDPE-*d*₄ was purchased from Cambridge Isotope Laboratories (DLM-220). HDPE 42,799-3, PP 42,818-3, LLDPE 42,809-4, LDPE 42,804-3, and E-co-B 43,473-6 were purchased from Aldrich.¹⁴ All were used as received except for the PP, which was extracted with toluene at 60 °C and precipitated into methanol to produce an atactic, amorphous polymer.

Sample Preparation and SANS

Samples were prepared by two methods: solution-mixed and melt-mixed. The solution-mixed samples were dissolved in xylene at 140 °C and precipitated into methanol. They were dried in vacuum and pressed at 150 °C into disks for SANS. The melt-mixed samples were pressed at 150 °C and folded twice and repressed. The folding and pressing was repeated 10 times.

SANS experiments were carried out on the 8m (NG1) and 30m (NG7) instruments of the National Institute of Standards Technology, Cold Neutron Research Facility in Gaithersburg, Maryland.²⁰ The wavelength λ of the incident beam was 6 Å. Two different configurations were used: $D_{ss} = 4.10$ m, $D_{sd} = 3.60$ m, and $D_{ss} = 3.92$ m, $D_{sd} = 1.30$ m for the NG1 and NG7 instruments, respectively (D_{ss} is the source-sample distance and D_{sd} is the sample-detector distance). These configurations correspond to a scattering of wavevectors q varying between $2 \times 10^{-2} \text{ \AA}^{-1} < q < 0.17 \text{ \AA}^{-1}$ (NG1) and $3.2 \times 10^{-3} \text{ \AA}^{-1} < q < 0.45 \text{ \AA}^{-1}$ (NG7) [with $q = (4\pi/\lambda)\sin(\theta/2)$, θ being the scattering angle]. The observed scattering intensity at a given temperature was collected over a two-dimensional detector and was corrected for empty cell, background radiation, and detector inhomogeneity. It is then normalized against H₂O, which serves as a secondary standard, to give the absolute intensity. Finally, it is circularly averaged to give the q dependence of the coherent scattering cross section, $d\Sigma/d\Omega(q)$, in absolute units (cm⁻¹). The uncertainties are calculated as the estimated standard deviation of the mean and the total combined uncertainty is not given as comparisons are made with data obtained under the same conditions. In cases where the limits are smaller than the plotted symbols, the limits are left out for clarity. Fits of the scattering data are made by a least-squares fit of the data giving an average and a standard deviation to the fit. All

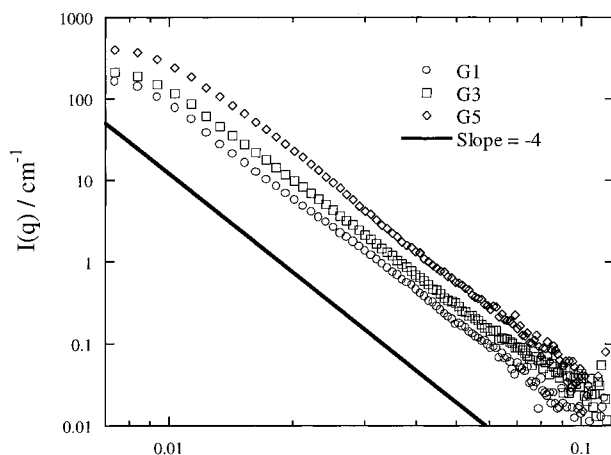


Figure 1. SANS from blends of mass fraction, 2% dendrimer-*h* in 98% mass fraction HDPE-*d*₄. ○, G1; □, G3; ◇, G5.

temperatures reported are within ± 1 °C as determined by previous experience.

RESULTS AND DISCUSSION

Differential scanning calorimetry was used to determine the melting points of the crystalline regions of the polyolefins so that blending and SANS could be carried out on amorphous samples. Miscible blends can be made to phase separate upon crystallization of one component. The highest melting point was for HDPE-*d*₄, which showed complete melting by 130 °C.²¹ Therefore all of the melt-mixing was carried out at 150 °C and the scattering was done at 140 °C.

The first set of experiments checked for miscibility of HDPE-*d*₄ with dendrimers of different size. Figure 1 is a plot of the SANS from binary blends of mass fraction, 2% dendrimer-*h* in HDPE-*d*₄. A log-log plot shows that there is an extensive region with a slope of q^{-4} .¹⁷ This is characteristic of Porod scattering from a morphology that is strongly phase-separated with negligible mixing within the phases and a negligible interfacial region between the phases. In this q range, there is no leveling off of the scattering intensity at low q . This extended range of power law behavior indicates that the characteristic size of the two phase morphology is larger than can be measured under these instrumental conditions.

Figure 2 is a Guinier plot of the scattering from blends of mass fraction, 2% dendrimer-*h* HDPE-*d*₄. The measurement was taken with the 8M

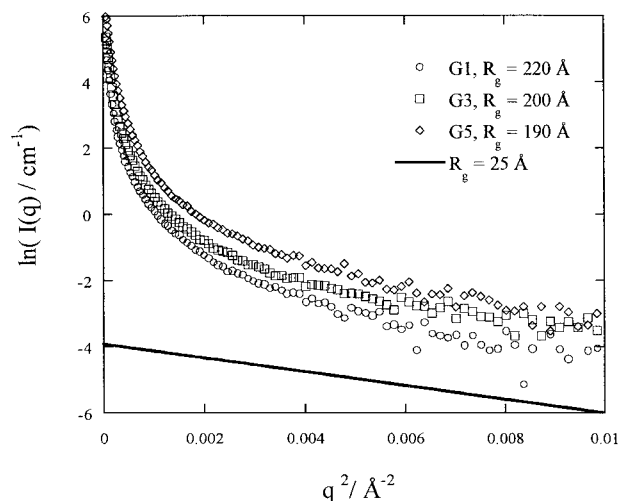


Figure 2. Guinier plot of the scattering from blends of mass fraction, 2% dendrimer-*h* in HDPE-*d*₄. ○, G1; □, G3; ◇, G5.

SANS instrument, which had a low q value of 0.008 \AA^{-1} . An estimate can be made of the characteristic phase size if data is available in the range $q R_g \ll 1$. As can be seen, there is still curvature in the lowest accessible q region, so fits in this region only give a lower bound of the phase size. The fits over a q range of $0.008 < q/\text{\AA}^{-1} < 0.012$ give $R_g = 220 \text{ \AA}$, 200 \AA , and 190 \AA for G1, G3, and G5 respectively. Since $q R_g > 1$ under these conditions, the measured size is limited by the instrument resolution. These sizes therefore represent a lower bound of the true phase size.

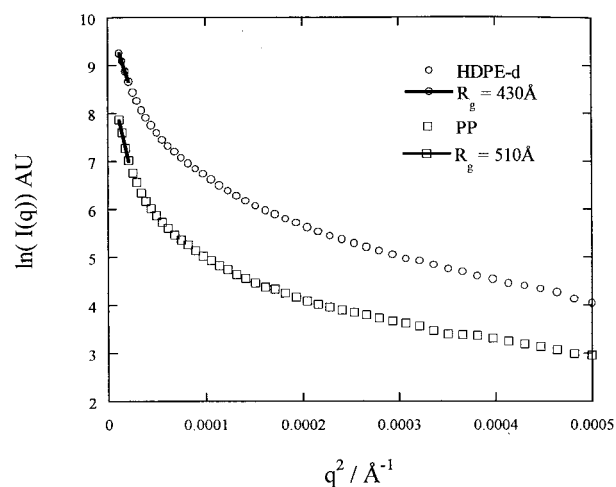


Figure 3. Guinier plot of 30 M SANS results from blends of mass fraction, 2% G5 dendrimer-*h* in HDPE-*d*₄, ○; and of 2% mass fraction G5 dendrimer-*d* in PP, □.

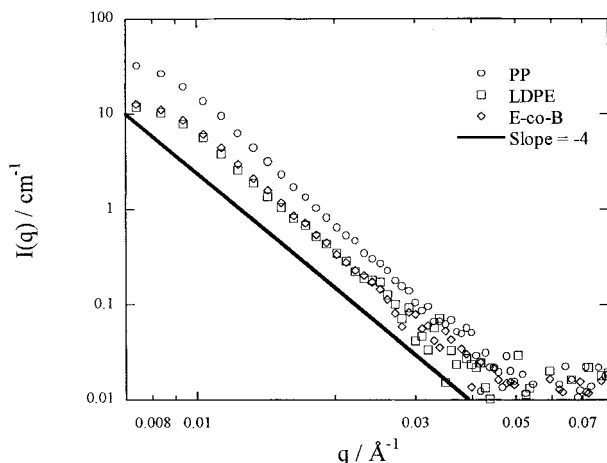


Figure 4. Mass fraction 2% G5 dendrimer-*d* in PP, ○; LDPE, □; and E-co-B, ◇.

Lower q data was collected to determine if a linear region could be achieved. Figure 3 is a Guinier plot of 30 M SANS results from blends of mass fraction, 2% G5 dendrimer-*h* in HDPE- d_4 and of mass fraction, and 2% G5 dendrimer-*d* in PP. Fits were made from $0.0032 < q/\text{Å}^{-1} < 0.0048$ giving $R_g = 430$, and 510 Å for G5-*h*/HDPE- d_4 and G5-*d*/PP, respectively. Again the condition $q R_g \ll 1$ is not held and there is considerable curvature, so that these represent minimum values. Since the R_g of a G5 dendrimer is less than 25 Å ,²² the dendrimer phases represent very large aggregates of dendrimers.

Other polyolefins were blended with dendrimers to see if miscibility was possible for other combinations. Figure 4 is a log-log plot of mass fraction, 2% G5 dendrimer-*d* in PP, LDPE, and E-co-B. As with the blends of PE described earlier, there is an extended region with a slope of q^{-4} , indicating strong phase separation. Since there is no plateau region at low q , as was the case of the other blends, these also have relatively large phase sizes, larger than the resolution of the SANS instrument. Also, the results shown are for both melt (LDPE, E-co-B) and solution processed (PP) samples with both giving identical power law scattering. No differences could be seen resulting from different preparation methods.

Crystallization of one or both components causes phase separation even in miscible blends.²³ While these blends were initially formed well above the melting temperature of all components, they were allowed to cool for transport and storage. If the phase separation due to the crystallization causes very large-size scale domains to

form, it is possible that the relatively short time of the SANS experiments did not allow enough time for remixing. To check this, blends were made from mass fraction, 98% amorphous PP. The only possible crystallinity would be in the mass fraction, 2% G5 dendrimer-*d*. SANS was carried out at 140 °C for 20 h without any lowering of the temperature.

Figure 5 shows the SANS from the blend at times of 5, 12, and 16 h. As with the other blends, there is an extended region with a slope of q^{-4} , indicating strong phase separation. Extended annealing of the blends does not change the scattering, showing that it is not a matter of crystallization-induced phase separation for this blend. For all of the blends, there was no indication of a consistent change in the scattering during the time of the SANS experiments, which typically was several h.

Figure 6 is a log-log plot of SANS results from binary blends of mass fraction, 2% G5 dendrimer-*h* in HDPE- d_4 and of mass fraction, 2% G5 dendrimer-*d* in HDPE- h_4 both below and above the crystalline melting point of the HDPE. Since the scattering length of C is $0.655 \times 10^{-12} \text{ cm}$, D is $0.667 \times 10^{-12} \text{ cm}$, and H is $-0.374 \times 10^{-12} \text{ cm}$, the repeat unit CH_2 is very near to zero, whereas that of CD_2 is large.²⁴ Upon crystallization, the change in specific volume causes the contrast factor of CD_2 to be large enough for the difference between the amorphous and crystalline regions to dominate the scattering, while for CH_2 , the amorphous and crystalline regions have virtually the

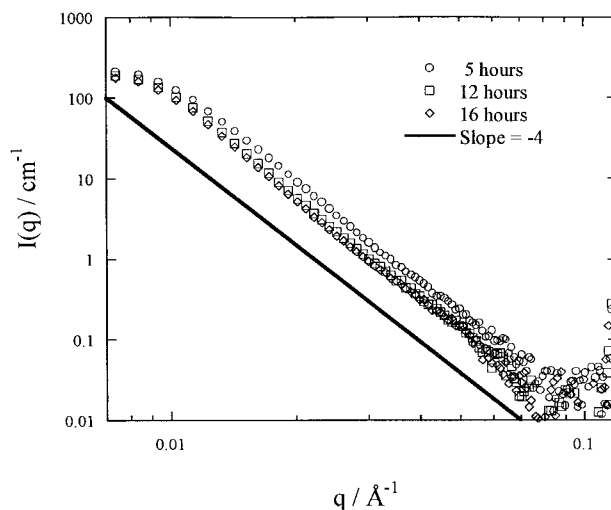


Figure 5. SANS from a blend of mass fraction, 98% amorphous PP and G5 dendrimer-*d* at average annealing times of 5, ○; 12, □; and 16 h, ◇ at 140 °C .

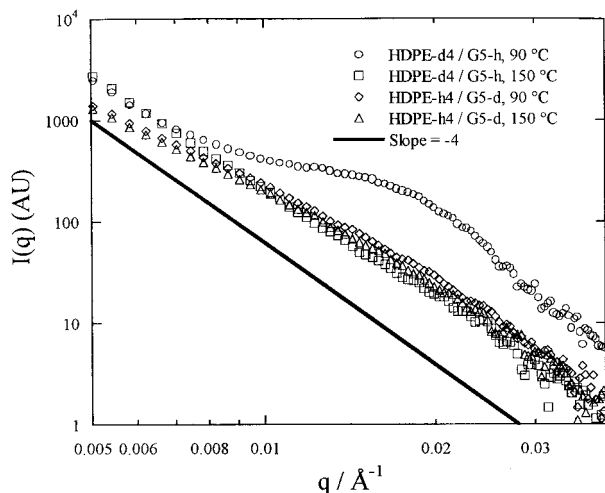


Figure 6. 30 M SANS results from blends of mass fraction, 2% G5 dendrimer-*h* in HDPE-*d*₄ above, ○, and below, □, the melting point; and of mass fraction, 2% G5 dendrimer-*d* above, ◇, and below, △, the melting point.

same contrast factor and the scattering is still dominated by the dendrimer. Figure 6 shows that the SANS from blends of mass fraction, 2% G5 dendrimer-*d* in HDPE-*h*₄ do not change above and below the melting point. This further demonstrates that crystallization does not affect distribution of the dendrimer phase.

CONCLUSIONS

Although melt-mixed samples of fatty acid modified PPI dendrimers appear transparent when kept above the melting temperature, SANS shows that they are actually phase-separated on a size scale much greater than the individual dendrimer size. This was true for all of the fatty-acid-modified dendrimers studied, G1, G3, and G5, in both hydrogen and deuterium forms. All polyolefins tested were immiscible with the dendrimers, HDPE, LDPE, PP, and E-co-B, in both hydrogen and deuterium forms. Melt-mixing by mechanical kneading of virgin material or with samples previously solution-mixed all produced immiscible blends. Premixing in solution also did not change the miscibility of the binary blends. Extended annealing did not produce any morphological changes in a size scale accessible to SANS.

The ultimate goal of blending fatty-acid-modified dendrimers is to promote long-term stability of additives to the polyolefins. Even if the size

scales of the dendrimer phase is relatively large, small molecules such as dyes that are permanently affixed to the dendrimers may be lodged in the polyolefin matrix. If this is the case, then the use of fatty-acid-modified dendrimers to promote long-term stability of additives may be applicable to a wide range of polymers other than polyolefins, independent of specific miscibility conditions.

The authors wish to acknowledge Drs. Josephine Brackman and Remko Vreekamp for their helpful discussions. This material is based upon work supported in part by the U.S. Army Research Office under contract number 35109-CH.

REFERENCES AND NOTES

- Tomalia, D. A.; Naylor, A. M.; Goddard III, W. A. *Angew Chem Int Ed Engl* 1990, 29, 138.
- Hawker, C. J.; Fréchet, J. M. *J Macromol* 1990, 23, 4726.
- Newkome, G. R.; Lin, X. *Macromolecules* 1991, 24, 1443.
- De Brabander-van den Berg, E. M. M.; Meijer, E. W. *Angew Chem* 1993, 105, 1370.
- Issberner, I.; Moors, R.; Vögtle, F. *Angew Chem* 1994, 106, 2507.
- Percec, V.; Chu, P.; Kawasumi, M. *Macromolecules* 1994, 27, 4441.
- Tomalia, D. A. *Adv Mater* 1994, 6, 529.
- Newkome, G. R. *Advances in Dendritic Macromolecules*; JAI Press: Greenwich, CT, 1993.
- Prosa, T. J.; Bauer, B. J.; Amis, E. J.; Tomalia, D. A.; Scherrenberg, R. *J Polym Sci Phys* 1997, 35, 2913.
- Jansen; J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* 1994, 266, 1226.
- Jansen; J. F. G. A.; Meijer; E. W. de Brabander-van den Berg, E. M. M. *J Am Chem Soc* 1995, 117, 4417.
- Stevelmans, S.; van Hest, J. C. M.; Jansen, J. F. G. A.; van Boxtel, D. A. F. J.; de Brabander-van den Berg, E. M. M.; Meijer, E. W., *J Am Chem Soc* 1996, 118, 7398.
- Froehling, P. E.; Linssen, H. A. *J Macromol Chem Phys* 1988, 199, 1691.
- Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for this purpose.
- Schenning, A. P. H. J.; Elissen-Roman, C.; Weener, J. W.; Baars, M. W. P. L.; van der Gaast,

- S. J.; Meijer, E. W. *J Am Chem Soc* 1998, 120, 8199.
16. PCT Pat Appl WO 97/19987, November 28, 1995.
17. PCT Pat Appl WO 98/12376, September 23, 1996.
18. Han, C. C.; Bauer, B. J.; Clark, J. C.; Muroga, Y.; Matsushita, Y.; Okada, M.; Tran-Cong, Q.; Chang, T. *Polymer* 1988, 29, 2002.
19. Higgins, J. S.; Benoit, H. In *Polymer and Neutrons Scattering*; Clarendon Press: Oxford, England, 1994.
20. Prask, H. J.; Rowe, M.; Rush, J. J.; Schroeder, I. G. *J Res Natl Inst Stand Tech* 1993, 8, 1.
21. Bates, F. S.; Keith, H. D.; McWhan, D. B. *Macromolecules*, 1987, 20, 3065.
22. Ramzi, A.; Bauer, B. J.; Scherrenberg, R.; Joosten, J.; Amis, E. J. *PMSE Preprints* 1998, 79, 382.
23. Crist, B.; Nicholson, J. C. *Polymer* 1994, 35, 1846.
24. *Neutron Cross Sections*, BNL 325, 3rd ed.; Garber, D. I.; Kinser, R. R., Eds.; Brookhaven National Laboratory, Upton, NY, 1976.