Table I
Glass Transitions in Blends of PPO with Polystyrene or Poly(α-methylstyrene)

	T_g, °C	
PPO wt fraction	PS blends	PMS blends
0.0	100	185
0.2	107-122	177-193
0.4	122-143	177-200
0.6	142-167	187-197
0.8	152-202	207-217
1.0	227	227

such an interpretation is greatly oversimplified. This is not surprising, since it has been known for a long time[17] that use of a single parameter (such as the cohesive energy density) to characterize the components of a mixture is inadequate for the prediction of the heat of mixing in systems in which dipole interactions are important, and this point has also been made specifically for the prediction of polymer compatibility.[18]

Table I lists the results of a DSC study of the PPO-PS and PPO-PMS systems. It may be seen that in both these systems a single glass transition temperature was detected for the various blends, so that calorimetry would have provided no evidence for a reduced compatibility when the styrene residues are methylated in the α position. The present study thus confirms our previous conclusion[2] that the energy transfer between fluorescent labels provides a more sensitive criterion of compatibility than calorimetric data.

Acknowledgment. We are grateful for financial support of this study by the National Science Foundation under Grant No. DMR-77-05210, Polymer Program.

References and Notes

(1) On a leave of absence from the Department of Polymers, Prague Institute of Chemical Technology, Prague 6, Czechoslovakia.
(2) F. Amrani, J. M. Hung, and H. Morawetz, *Macromolecules*, **13**, 649 (1980).
(3) T. Förster, *Discuss. Faraday Soc.*, **27**, 7 (1959).
(4) J. Stoelting, F. E. Karasz, and W. J. MacKnight, *J. Polym. Eng. Sci.*, **10**, 133 (1970).
(5) A. R. Shultz and B. M. Gendron, *J. Appl. Polym. Sci.*, **16**, 461 (1972).
(6) P. Alexandrovich, F. E. Karasz, and W. J. MacKnight, *J. Appl. Phys.*, **47**, 4251 (1976).
(7) P. Alexandrovich, F. E. Karasz, and W. J. MacKnight, *Polymer*, **18**, 1022 (1977).
(8) H. E. Weeks, F. E. Karasz, and W. J. MacKnight, *J. Appl. Phys.*, **48**, 4068 (1977).
(9) G. D. Jones, *Ind. Eng. Chem.*, 44, 2686 (1952).
(10) H. W. Gibson and F. C. Bailey, *Macromolecules*, **9**, 688 (1976).
(11) M. E. Tate and C. T. Bishop, *Can. J. Chem.*, **41**, 1800 (1963).
(12) S. J. Cristol, J. W. Ragsdall, and J. S. Meek, *J. Am. Chem. Soc.*, **71**, 1863 (1949).
(13) L. M. Robeson, M. Matzner, L. J. Fetters, and J. E. McGrath, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **No. 14**, 1063 (1973); "Recent Advances in Polymer Blends, Grafts and Blocks", L. H. Sperling, Ed., Plenum Press, New York, 1974, p 281
(14) D. J. Dunn and S. Krause, *J. Polym. Sci., Part B*, **12**, 591 (1974).
(15) (a) W. J. MacKnight, J. Stoelting, and F. E. Karasz, *Adv. Chem. Ser.*, **No. 99**, 29 (1971); (b) W. M. Prest, Jr., and R. S. Porter, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 1639 (1972); (c) A. R. Shultz and B. M. Beach, *Macromolecules*, **11**, 158 (1978).
(16) R. E. Wetton, W. J. MacKnight, J. R. Fried, and F. E. Karasz, *Macromolecules*, **11**, 158 (1978).
(17) J. H. Hildebrand and R. L. Scott, *ACS Monogr.*, **No. 17**, 162-9 (1950).
(18) M. T. Shaw, *J. Appl. Polym. Sci.*, **18**, 449 (1974).

Low-Temperature Crystallization of Poly(dimethylsiloxane) from Solution

P. R. Sundararajan,* G. K. Hamer, and M. D. Croucher

Xerox Research Centre of Canada, 2480 Dunwin Drive, Mississauga, Ontario L5L 1J9, Canada. *Received January 22, 1980*

ABSTRACT: Poly(dimethylsiloxane) (PDMS) has been crystallized from solution in hydrocarbons at about −90 °C. It is shown that the temperature of crystallization is independent of the hydrocarbon medium. X-ray diffraction studies show the degree of crystallinity of the low molecular weight PDMS to be greater than that of the high molecular weight material. Proton NMR has been used to detect the phase separation and to confirm the X-ray observations. It is shown that the crystallization of PDMS from solution is a bulk phenomenon and not surface-induced.

It has recently been reported[1,2] that poly(methyl methacrylate) particles that are stabilized by poly(dimethylsiloxane) (PDMS) flocculate both on heating and on cooling when dispersed in *n*-alkanes. The upper critical flocculation temperature (UCFT) was found to correlate qualitatively with the Θ temperature associated with the lower critical solution temperature (LCST) of the respective PDMS + *n*-alkane solutions.[3,4] However, the lower critical flocculation temperature (LCFT) was found to be essentially independent of the nature of the dispersion medium and occurred at a temperature far above the Θ temperature associated with the upper critical solution temperature (UCST) that has been estimated for these solutions.[5] It has been suggested[6] that the LCFT in these systems is due to surface-induced crystallization of PDMS, which allows the attractive van der Waals forces between the particles to become operative, thereby causing the particles to flocculate. It has been shown recently,[7] from low-temperature X-ray diffraction studies on PDMS-stabilized particles, that crystallization of PDMS occurs at about −90 °C, well above the suggested Θ temperature of about −173 °C for these systems.[5]

In order to investigate the requirement of the presence of a particle surface for the crystallization of PDMS to occur, we have carried out low-temperature X-ray and NMR measurements on PDMS, dissolved in two hydrocarbon liquids. We report the first measurements on the crystallization behavior of PDMS from solution, which is

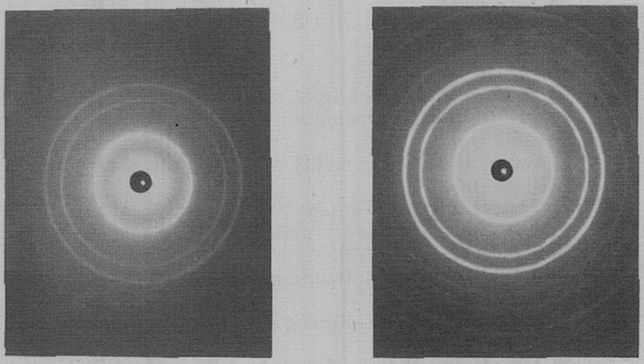

Figure 1. X-ray diffraction patterns from solution-crystallized PDMS samples at about −90 °C: (a) corresponds to samples with $M_w = 544\,000$ and $M_w = 76\,760$; (b) corresponds to sample with $M_w = 7400$.

found to occur in the range of −75 to −100 °C.

Experimental Section

Three samples of PDMS were obtained from Petrarch Corp. The molecular weights as measured by GPC were $M_w = 544\,000$ ($M_w/M_n = 2.31$), $M_w = 76\,760$ ($M_w/M_n = 1.90$), and $M_w = 7400$ ($M_w/M_n = 1.32$). Proton NMR showed that the samples with $M_w = 544\,000$ and 7400 contained about 10% of low molecular weight siloxanes. The solubility of the samples in *n*-alkanes confirmed that the material was a linear polymer. The X-ray patterns were recorded for the three samples, using a 10.4 wt % solution of PDMS in *n*-heptane; a 10.8 wt % solution of PDMS ($M_w = 544\,000$) in toluene/toluene-d_8 (see below) was also examined. The solutions were filled in a glass capillary (0.5-mm diameter, Philips Electronics Ltd.) mounted on a eucentric goniometer head, which was placed on the floor of a box camera (W. Warhus & Co.). The capillary was positioned close to the collimator of 0.02-in. diameter. The box camera itself was insulated by wrapping several layers of fiberglass around it. Air from the laboratory air line was passed through a serpentine coil immersed in liquid nitrogen and was circulated through the camera. The temperature was controlled by adjusting the air flow rate and was measured by a thermocouple placed close to the sample. The exposure (Cu Kα radiation) was started after equilibrating the sample for 2 h at the chosen temperature. The patterns were recorded on a flat-plate cassette. The bulk samples of PDMS were irradiated for the same period of time as the solutions and were subsequently dissolved in *n*-heptane to confirm the absence of radiation-induced cross-linking in these samples.

Proton NMR spectra were recorded for a 10.8 wt % solution of PDMS ($M_w = 544\,000$) in toluene/toluene-d_8 (1:7), using a Bruker WP-80 Fourier transform spectrometer operating at 80 MHz. The sample was contained in a 4.2-mm inner diameter NMR tube (Wilmad Glass Co.). The probe temperature was controlled (±1 °C over the range from +32 to −90 °C) with a Bruker B-VT-1000 digital temperature regulator, calibrated against neat methanol according to the method of Van Geet.[8] Approximately 15 min was allowed for thermal equilibration at each temperature setting. Spectra were integrated digitally with the Bruker FTQNMR program, using the toluene methyl group signal as an internal integration standard; the results were normalized to the PDMS/toluene integral ratio recorded at ambient temperature (32 °C).

Results and Discussion

X-ray diffraction studies[9] on silicone rubbers have shown that crystallization occurs at about −60 °C. Stretching the rubber initiates oriented crystallization at a temperature of about −30 °C, the degree of crystallinity increasing with a decrease in temperature. Unit-cell dimensions of a = 13.0 Å, b = 7.75 Å, c (chain axis) = 8.3 Å, and $\gamma = 60°$ were derived by Damaschun,[10] using a fourfold-stretched silicone rubber at −90 °C.

Table I
Observed and Calculated Interplanar Spacings of Reflections[a] for PDMS Crystallized from Solution[b]

d(obsd), Å	d(calcd), Å	hkl indices
6.80	6.71	010
4.11	4.15	002
3.54	3.53	320, 210, 012
2.97	2.99	312
2.71	2.69	121, 322, 212, 103
2.40	2.40	220, 113
2.26	2.25	223
2.07	2.08	222, 004
1.99	2.00	130, 321, 403, 123 114, 014

[a] From Figure 1b. [b] Using the unit-cell dimensions proposed by Damaschun,[10] but with c as the chain axis.

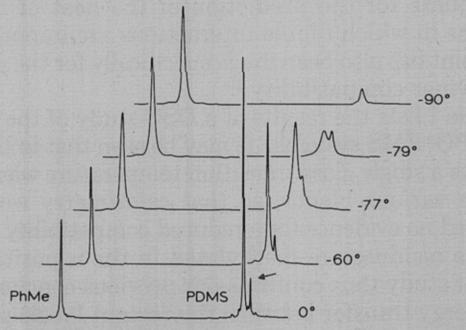

Figure 2. ^{1}H NMR (80 MHz) spectra of the methyl group peaks of PDMS + toluene recorded at the temperatures shown. The arrow indicates low molecular weight siloxane species present in the PDMS sample.

The X-ray patterns for the samples crystallized from solution in *n*-heptane are shown in Figure 1. All three samples crystallize from solution in the range −90 to −100 °C. Small variations were observed in the temperature of crystallization, but these were within the experimental error and, thus, cannot be reliably correlated with the molecular weight. However, it is seen from Figure 1 that, while the polymers with $M_w = 544\,000$ and 76 760 show three Debye–Scherrer rings, as in the previous studies on silicone rubbers,[10] the sample with $M_w = 7400$ shows as many as nine reflections and is qualitatively more crystalline. The interplanar spacings of the reflections and their Miller indices are given in Table I. It is interesting to note that the spacings derived here for linear PDMS crystallized from solution and cross-linked PDMS used in previous studies[9,10] are the same, indicating the absence of differences in the molecular conformation or structure. The pattern for the sample with $M_w = 544\,000$ crystallized from toluene is identical with that given in Figure 1a and occurs at about −90 °C. This lends support to the previous observation[1] that the LCFT was essentially independent of the nature of the hydrocarbon dispersion medium.

One of the questions of interest is whether the crystallization of PDMS from solution at about −90° C is induced by the presence of the glass surface of the capillary used for recording the X-ray data. NMR spectroscopy, rather than turbidity methods, was used to examine this possibility. The bore of the NMR sample tube was 4.2-mm internal diameter, in contrast to the 0.5-mm diameter of the X-ray capillary.

Representative spectra of PDMS ($M_w = 544\,000$) in toluene, recorded at several temperatures, are shown in Figure 2. A plot of the normalized integrated intensity of the PDMS peak (relative to that of the toluene methyl peak) as a function of temperature is shown in Figure 3. It is evident that the intensity of the PDMS peak decreases

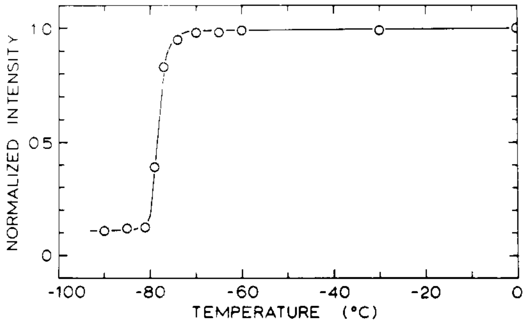

Figure 3. Normalized integrated peak intensity of PDMS, relative to the methyl group intensity of toluene, as a function of temperature.

rapidly below −70 °C, vanishing almost completely at −80 °C. The small peak which remains is due to low molecular weight species present in the sample and is indicated by the arrow in Figure 2. This behavior, which is reversible, is indicative of a disorder–order transition, i.e., crystallization of PDMS. The "crystallization temperature" is relatively sharp. However, the phenomenon is rate-dependent; i.e., it depends on the time allowed for equilibration at each temperature.[11]

Both NMR and X-ray measurements show that the crystallization of PDMS from solution in toluene occurs between −75 and −90 °C. It should be noted that this temperature is much lower than the temperature of −37 °C, corresponding to the UCST, predicted for the PDMS + toluene system by Kuwahara et al.[5] It is seen from Figure 3 that there is no indication of a phase separation in the region from −30 to −40 °C, nor was there any visual evidence of phase separation above −75 °C.

Conclusions

It has been shown that the crystallization of PDMS from solution occurs between −75 and −100 °C. The interplanar spacings for the solution-crystallized PDMS and the cross-linked silicone rubbers are identical. The lower the molecular weight, the greater is the degree of crystallization, as can be seen from the number of reflections recorded in Figure 1. The results indicate that crystallization of PDMS from solution is a bulk phenomenon and not surface-induced as was previously suggested.[6] It would also appear that the Θ temperature predicted in the literature for the PDMS + toluene system should be reevaluated.

Acknowledgment. We are indebted to Dr. M. L. Hair for interesting discussions and to L. C. Campbell for recording the low-temperature X-ray patterns.

References and Notes

(1) D. H. Everett and J. F. Stageman, *Colloid Polym. Sci.*, **255**, 293 (1977).
(2) D. H. Everett and J. F. Stageman, *J. Chem. Soc., Faraday Discuss.*, **65**, 230 (1978).
(3) D. Patterson, G. Delmas, and T. Somocynsky, *Polymer*, **8**, 503 (1967).
(4) L. Zeman, J. Biros, G. Delmas, and D. Patterson, *J. Phys. Chem.*, **76**, 1206 (1972).
(5) N. Kuwahara and M. Kaneko, *Makromol. Chem.*, **82**, 205 (1965).
(6) M. D. Croucher and M. L. Hair, *Macromolecules*, **11**, 874 (1978).
(7) M. D. Croucher, M. L. Hair, and P. R. Sundararajan, *Colloid Polym. Sci.*, in press.
(8) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970).
(9) S. M. Ohlberg, L. E. Alexander, and E. L. Warrick, *J. Polym. Sci.*, **27**, 1 (1958).
(10) G. Damaschun, *Kolloid Z.*, **180**, 65 (1962).
(11) L. Mandelkern, "Crystallisation of Polymers", McGraw-Hill, New York, 1964.

Thermally Stimulated Depolarization of Phase-Separated Polymer Systems

J. Vanderschueren,* M. Ladang, and J. M. Heuschen[†]

Département de Chimie Physique et Département de Chimie Macromoléculaire et Catalyse Organique, Université de Liège, Sart-Tilman, B 4000 Liège, Belgium.

Received November 28, 1979

ABSTRACT: The thermally stimulated depolarization method has been used to study the relaxation behavior of the two block copolymers poly(styrene-*b*-butadiene) and poly(ϵ-caprolactone-*b*-styrene) and the polyblend poly(methyl methacrylate)–poly(*tert*-butyl acrylate). The relaxation peaks resulting from molecular local motions or glass transition are similar to those observed in pure homopolymers, showing that a well-defined phase separation occurs in these systems. In addition, peaks due to interfacial polarization are obtained where the constituent phases possess markedly different electrical conductivities while no evidence is found for a relaxation effect requiring the existence of a diffuse interface between the microdomains.

It is known that the relaxational behavior of block copolymers and polyblends in the solid state is largely determined by their microdomain morphology: if the boundary between phases is sharp, the molecular relaxation spectrum can be, in principle, strictly described by a superposition of the spectra of the two pure homopolymers; if a more or less important amount of molecular mixing is taking place, the transitions are generally broadened, their maximum temperatures are closer together, and new relaxation peaks may appear. In these conditions, a current and essential problem encountered in the study of the multiphase systems is to determine the cause and nature of the influence of one particular material on the other's relaxation. With this in view, dynamic mechanical characteristics, mostly in the form of the temperature response of shear or Young's modulus and mechanical loss, have been used with considerable success.[1-3] The dielectric measurements, in particular the temperature dependence of dielectric constant and losses, were also shown to be a useful means for characterizing the nature of phase separation because they allow not only the fol-

---

[*] Chargé de Recherches du Fonds National de la Recherche Scientifique (Belgium).

[†] Département de Chimie Macromoléculaire et Catalyse Organique.

0024-9297/80/2213-0973$01.00/0