Effects of solvent and thermal annealing on the dielectric properties and morphology of dimethyl siloxane/α-methylstyrene block copolymers

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The dielectric and morphological properties of a series of 9/1 poly(dimethyl siloxane) (PDMS)/poly(α-methylstyrene) (PαMS) block copolymers and a 6/4 PDMS/PαMS block copolymer have been determined as a function of solvent casting and thermal treatment. Transmission electron microscope (*TEM*) results show better phase separation as a function of thermal annealing and casting from cyclohexane, a PDMS preferential solvent. Dielectric studies in the temperature region of the PDMS glass transition are consistent with the *TEM* results and are interpreted in terms of a most probable distribution of PDMS/PαMS mixed states. When the PDMS segment molecular weight is less than the critical molecular weight, thermal annealing of the solvent cast samples produces a phase separated sample exhibiting the T_g of PDMS as well as a mixed phase. Thermal annealing of samples with the PDMS segment molecular weight greater than the critical molecular weight produces little change in the mixed structure and the dielectric data. All samples have PαMS segment molecular weights less than the critical molecular weight. The observed changes are interpreted in terms of kinetic effects associated with polymer melt viscosity (critical molecular weight) and expected mixing of the two components.

INTRODUCTION

Block copolymers are interesting materials because similar or dissimilar polymer segments can be incorporated into single polymer molecules. A variety of morphologies can be obtained from these copolymers by varying their composition, the compatibility of the homopolymers comprising the copolymer and by judicious choice of coating solvent[1-6]. The various morphologies effect ultimate mechanical properties[1] as well as dynamic mechanical[7] and dielectric properties[5,8,9]. Many of these properties have been explained in terms of pure segment domain morphologies coupled by small mixed interface regions between the domains.

Recently there has been much discussion of the nature and significance of the domain boundary between immiscible polymers or block copolymers containing immiscible components[10-15]. Kraus has shown that the degree of phase separation is controlled by the composition of each block and is maximized at a statistical 50/50 composition[16,17]. In addition, the composition of the interpenetration layer is a function of, among other parameters, sample preparation methods, sample molecular weights, segment molecular weights, casting solvents, types of multiblock structure, and mutual solubilities of polymer segments[18,19]. In cases where interphase mixing is great, dynamic relaxations due to the mixed state are observed. This is discussed for poly(dimethyl siloxane) (PDMS)/bisphenol-A carbonate block copolymers by Kaniskin *et al.*[8]. More recently Kraus *et al.*[10] have shown in dynamic mechanical studies of styrene/butadiene triblocks that even though large asymmetric interfacial (or mixing) volumes exist and are dissimilar to bulk compositions, intermediate mixing relaxations need not be observed. In order to better understand the effect of composition and molecular weight on interfacial mixing and provide a broader base for

theoretical considerations, a study of the effect of solvent and thermal annealing on the morphology and dielectric relaxation spectra of two series of PDMS/α-methylstyrene (PαMS) block copolymers has been undertaken. One series of block copolymer samples varies in chemical composition. Another series varies in segment molecular weight at constant composition, so that effects such as critical molecular weight can be studied.

EXPERIMENTAL

Block copolymer samples

Samples of the PDMS/PαMS block copolymers were obtained from Dow Corning. The polymers are listed in *Table 1* with molecular weights and compositions reported by Dow. The elemental analysis for 6/4 PDMS/PαMS agreed with this proportion of PDMS to PαMS. The elemental analysis for 9/1 PDMS/PαMS indicated a PDMS to PαMS ratio of 8.5:1.5. Analysis for 6/4 PDMS/PαMS: C, 56.95%; H, 8.15%; Si, 23.58%. Calculated: C, 56.0; H, 8.30; Si, 22.7. Analysis for 9/1 PDMS/PαMS: C, 41.44; H, 8.07; Si, 32.02. Calculated: C, 38.35; H, 8.15; Si, 34.0.

Degradation of 9/1 PDMS/PαMS

A mixture of 40 g KOH, 90 g distilled H_2O, 270 g ethanol, 50 g benzene, and 40 g 9/1 PDMS/PαMS was refluxed for 6–7 days. The mixture was evaporated to dryness, dissolved in 250 ml of benzene and extracted with two 500 ml portions of distilled water. Both water layers were extracted with benzene. The benzene extracts were condensed to ~50 ml and added dropwise to a ten-fold excess of hexane to precipitate poly(α-methylstyrene). The resulting white powder was filtered and dried *in vacuo* over-

Table 1 Compositional data and designations for PDMS/PαMS block copolymers

Designation	PDMS (wt %)	$\bar{M}_n$(PαMS)	$\bar{M}_w$(PDMS)	$\bar{M}_w$ (PDMS) > $\bar{M}_c$ (PDMS)
6/4	60	8020	12 000	No
9/1 (3K)	90	3000	27 000	No
9/1 (6.5K)	90	6500	58 500	Yes
9/1 (11K)	90	11 000	99 000	Yes
9/1 (22K)	90	22 000	198 000	Yes

night to give 6.0 g. This is a 98.4% yield based on the 15.3 wt % α-methylstyrene content in the block copolymer obtained from elemental analysis. The infra-red spectrum showed the lack of siloxane peaks at 1000 and 800 cm^{-1}. Analysis: C, 91.45%; H, 8.22%; Si, 0.34%; Ash, 0.70%. Calculated for C_9H_{10}: C, 91.47%; H, 8.53%; Si, 0.00%.

Measurements

I.r. measurements were carried out on a Beckman 4024 IR spectrophotometer. Gas chromatography analyses were carried out on a Hewlett—Packard gas chromatograph using columns containing 10% OV-1 on 60/80 Supelcoport. Contact angle measurements were obtained with ethylene glycol using a Ramé-Hart, Inc., Contact Angle Goniometer Model A-100. Differential scanning calorimetry measurements were obtained on a Perkin—Elmer DSC-1B in a temperature range from 273 to 498K. Optical experiments were performed on a Bausch and Lomb, Trans-illumination Microscope or a Leitz Wetzlar Microscope.

All experiments on the copolymers were conducted on samples cast onto aluminium, glass or copper transmission electron microscope (*TEM*) grids from xylene, a mutual solvent for the block components, or cyclohexane, a PDMS preferential solvent. Samples were quickly dried for ~1–2 min, examined and then were heated at 498°C for 30 min and examined again. Chemical staining was not necessary because the large electron density differences between the block copolymer components resulted in dark spots on the *TEM* photomicrographs for PDMS phases and light spots for PαMS phases.

For dielectric measurements the above films were additionally vacuum dried (10^{-3}mmHg) for at least 24 h at room temperature and then gold electrodes were evaporated onto an exposed surface. Contact wires were attached with ECCO Shield conducting epoxy. Samples were isolated from the environment in a stainless steel box sealed with Teflon®. A thermocouple was mounted through a hole in the box to be within a centimeter of the sample surface. The thermocouple was sealed into the box with epoxy resin. Calibration with known standards indicated the temperature to be within ±2K of the thermocouple readings.

Dielectric data were obtained with an automatic recording instrument which has been described previously[20,21]. The system consists of a General Radio 1683 Automatic RLC Bridge and Doric Digital Thermocouple coupled to a multiplex system which cues the measuring devices, receives data in parallel bits of information and transfers data in ASCII code to a magnetic tape recording instrument. The data is then transferred via phone to a computer and processed. Resolution of the instrument is a function of the capacitance being measured and is approximately ±1% in our experiments. Baseline noise can be observed with very small tan δ (10^{-3}) as can be seen in *Figure 3a*. Temperature is controlled

by a Delta Design environmental oven which is capable of isothermal or temperature scanning experiments to 0.1K accuracy. Dielectric experiments were carried out at a scanning rate of 0.9 K/min at 120 Hz.

RESULTS AND DISCUSSION

Sample characterization

The molecular weights and compositions of the block copolymers used in this study as reported by Dow Corning are given in *Tables 1* and *2*. The 9/1 (6.5K) polymer was checked by independent analysis. The Si content determined by elemental analyses and the total $\bar{M}_n$ determined by membrane osmometry in toluene were close to reported values. As samples were prepared anionically, a monodisperse molecular weight distribution for each segment is approached. Therefore, the $\bar{M}_n$ for each segment is about equal to the $\bar{M}_w$. The gel permeation chromatogram (g.p.c.) did not have distinct multinodal or binodal molecular weight distributions, indicating that a good separation of block copolymer from the homopolymer reactants was obtained. The molecular weight distribution (*Table 3*) was polydisperse as expected for the random coupling of monodisperse or polydisperse polymers. A sample of PαMS, isolated from an alcoholic KOH hydrolysis medium which degraded the siloxane portion of 9/1 6.5K, had $\bar{M}_n$ somewhat higher than the reported value. The g.p.c. for PαMS displayed an almost monodisperse molecular weight distribution as expected for an anionically prepared polymer. The silicon analysis of the isolated PαMS was very low (0.34% Si) and the i.r. spectrum showed the lack of the characteristics Si—O absorption peaks at 800 and 1000 cm^{-1}.

An extensive gas chromatographic analysis for residual solvent was undertaken to determine whether or not plasticizing solvents were present to facilitate segment migration in these block copolymers. For thin film (20–60 μm) samples, cast from xylene, whether thermally treated or not, no detectable quantity (⩾0.5% wt) of xylene was found within 24 h after casting. The limit was determined by the external addition of known quantities of xylene to the sample solutions.

Thermal cycling did not cause chemical decomposition, oxidation, crosslinking or other chemical modifications of the block copolymer as determined by i.r. spectroscopy and

Table 2 Characterization data for 9/1 (6.5K)

	Dow corning	Our analyses
PDMS Content	90 wt %	85 wt %[1]
PαMS Content	10 wt %	15 wt %[1]
Total $\bar{M}_n$	237 000	254 000[2]
PαMS $\bar{M}_n$	6580	10 300[3]

[1] Calculated from elemental analysis data; [2] membrane osmometry in toluene at 36°C; [3] membrane osmometry in amyl acetate at 36°C

Table 3 G.p.c. data for 9/1 (6.5K) and PαMS

Material	Conditions	$\bar{A}_w$	$\bar{A}_n$	$\bar{A}_w/\bar{A}_n$
9/1 (6.5K)	THF at 27°C	9260	2370	3.91
PαMS[a]	CHCl$_3$ at room temperature	304	235	1.29

[a] Isolated from 9/1 PDMS/PαMS by basic hydrolysis

Table 4 G.p.c. and intrinsic viscosity data for thermally treated and untreated 9/1 (6.5K) and 6/4 samples

Material	Thermal treatment	G.p.c.			Intrinsic viscosity[2] (dl/gm)
		$\bar{A}_w$	$\bar{A}_n$	$\bar{A}_w/\bar{A}_n$	
9/1 (6.5K)	None	8750	2710	3.23	1.52
9/1 (6.5K)	30 min/225°C	8960	2680	3.35	1.46
6/4	None	4020	1410	2.86	0.70
6/4	30 min/225°C	4250	1440	2.95	0.74

[1] In THF at room temperature (~20°C); [2] in THF at 25°C
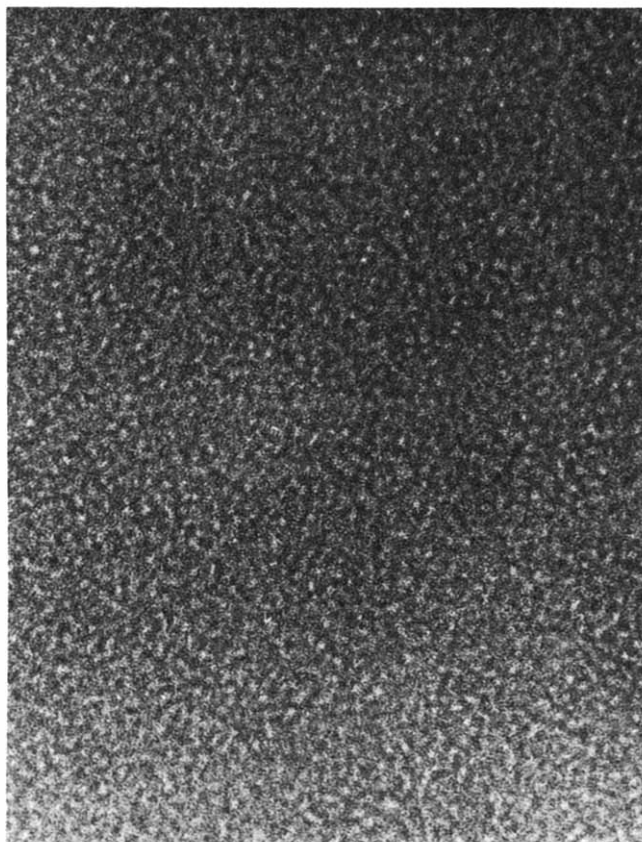
Figure 1 Transmission electron micrograph of 9/1 (11K) cast from cyclohexane. Magnification = 200K

molecular weight analysis. The infra-red and attenuated total reflectance infra-red spectra (measurement of the top 1 μm of material) of thin films of 9/1 and 6/4 materials as a function of heat treatment time (0 to 50 min) at 498K were identical. The intrinsic viscosity and g.p.c. data (*Table 4*) did not significantly change upon thermal treatment and, therefore, indicated that these materials experienced essentially no molecular weight changes.

Other techniques were used in attempts to characterize the effects of the thermal treatment in terms of thermodynamic changes and solvent plasticization. The thermal treatment had no effect on the differential scanning calorimetry data for these materials. The T_g for the α-methylstyrene segments was not observed either before or after heat treatment when using high sensitivity and large samples.

Contact angles for ethylene glycol on PDMS and PDMS/PαMS were identical and did not vary as a function of processing conditions or thermal treatment. This indicated that the top surface (first molecular monolayer) consisted primarily of silicone groups regardless of processing conditions.

Transmission electron microscopy (TEM)

Typical morphological results (*TEM*) for the block systems are shown in *Figures 1* and *2*. The dark and light domains correspond to PDMS and PαMS, respectively. The morphologies observed in solvent cast samples via *TEM* were obtained after rapid solvent evaporation and are not equilibrium structures. In the case of the thermally annealed samples the observed morphologies, or the changes from the morphology of the initially cast films, are probably indicative of the equilibrium morphology at 498K, since rapid cooling after annealing would inhibit any further changes in the samples. In comparing solvent induced morphologies, expected results were obtained; samples cast from preferential solvents exhibited a better defined granular structure as witnessed by the small dark domains in *Figure 1* than their mutual solvent counterparts. In samples of higher molecular weight, a supramolecular structure, an apparent aggregation of the granular structure, was also observed. An example of the granularity and suprastructure is shown in *Figure 1*. Thermal annealing of all samples (T = 498K for 30 min) above the glass transition of both copolymer components decreased the observed suprastructure content and promoted better phase separated domain structures. In some cases (*Figure 2*) a second suprastructure indicated by very dark random areas was introduced. These very dark areas could be PDMS-enriched domains or pinholes generated from very thin portions of the samples. Otherwise, the morphological results as a function of solvent and thermal cycling were as
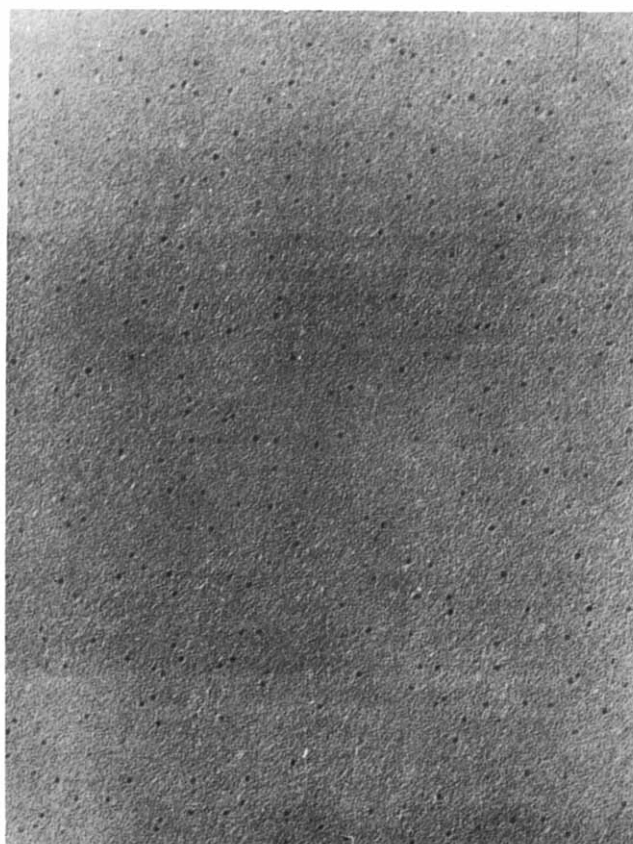

Figure 2 Transmission electron micrograph of 9/1 (3K) cast from cyclohexane. Magnification = 200K, thermally annealed at 498K' 30 min
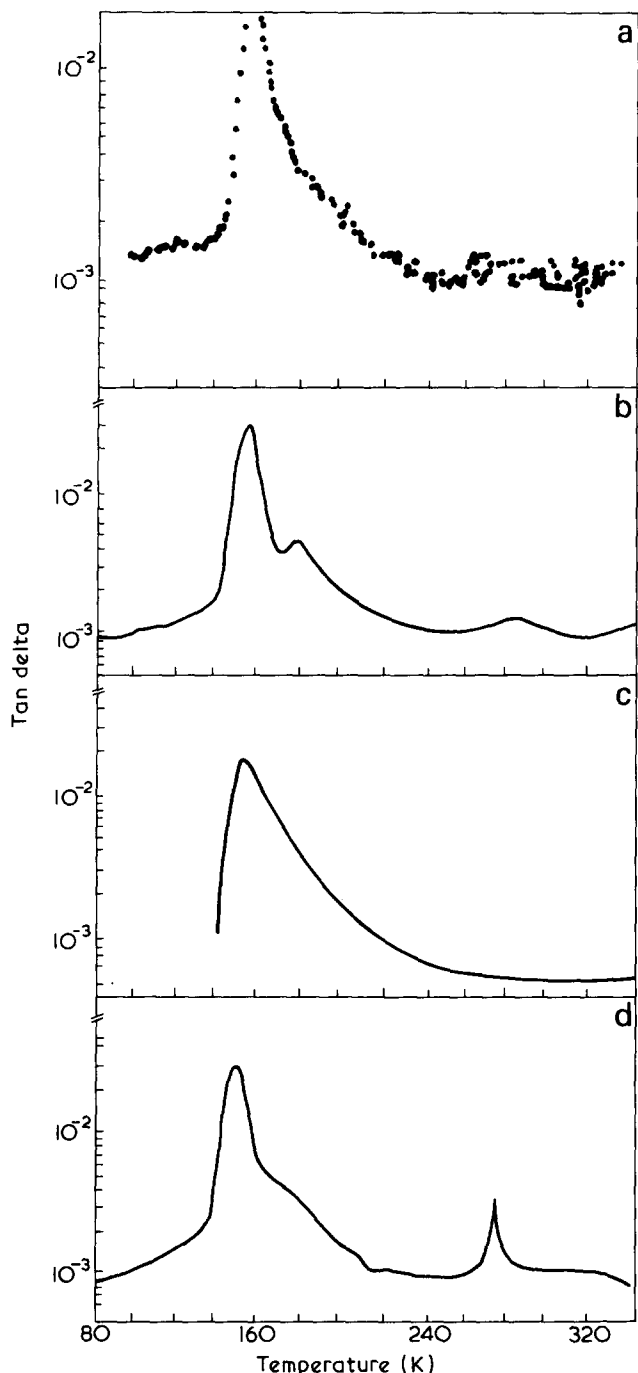
Figure 3 Tan δ *versus* temperature for a 6/4 sample: (a) cast from xylene; (b) annealed xylene sample; (c) cast from cyclohexane; (d) annealed cyclohexane sample

expected and very similar to those of Saam et al.[22] for polystyrene–PDMS ($\bar{M}_n$ (PDMS) = 7060, 28% PDMS) blocks cast from toluene.

Dielectric properties

A computer output of a typical dielectric scan is shown in *Figure 3a*. The remainder of the dielectric data (*Figures 3–8*) are presented as smoothed curves. In each case the maxima correspond to the glass transition temperature (T_g) of PDMS (155K) and, where present, the T_g of PαMS (420K). An additional peak is sometimes observed at 180K after thermal annealing or selective solvent casting (*Figures 3–5*). Additional small peaks are also occasionally observed in these spectra but are not considered for analysis because

they are either due to condensed water (this has been experimentally verified) on the sample (*Figure 3d*, peak at 270K) or are irreproducible (*Figures 5b* and *6b*, peaks in region of 210 to 320K). Since thermal annealing is done at 498K, the thermally cycled samples exhibit equilibrium morphologies characteristic of that temperature rather than room temperature. Even the 'as cast' samples must be considered to have been annealed at room temperature prior to testing. The high resolution of the dielectric instrument can be observed in *Figures 4–7*. Neither block copolymer component is very polar and yet the relaxations are readily discernible. With the exception of the 6/4 sample, all samples in these experiments failed at >340K and data are only shown for the temperature region from 80 to ~340K. The samples used in these experiments were thin and soft and in many cases high temperature measurements could not be made because the spring loaded configuration of our system caused catastrophic electrical failure of the samples. Many of the samples also had morphologies which did not permit electrode coating without shorting the samples (sample discontinuity). In these cases, dielectric experiments could not be conducted.
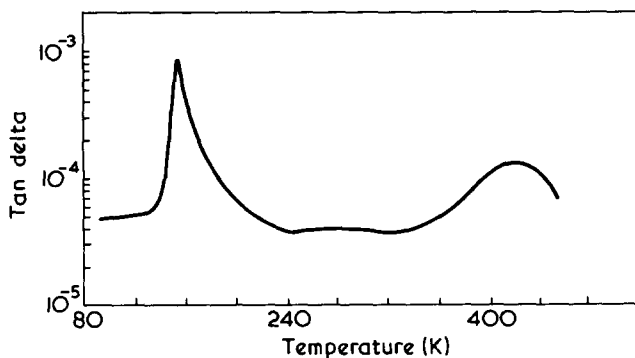

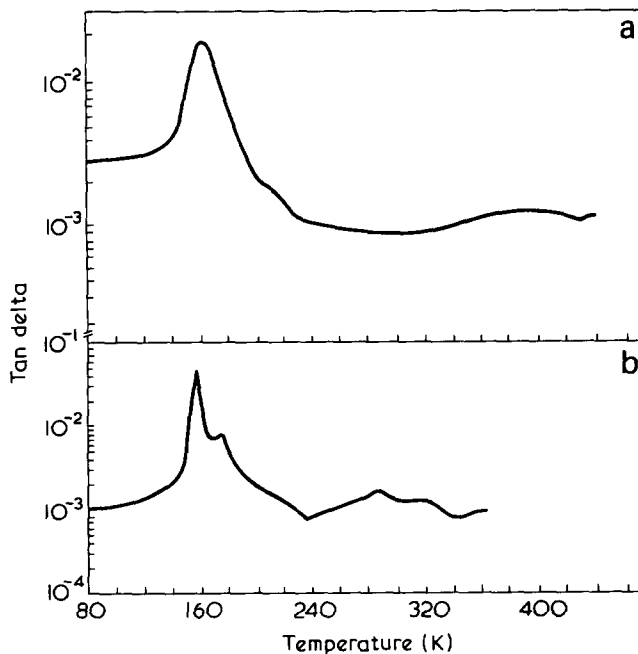*Figure 4* Tan δ *versus* temperature for a 6/4 sample cast from xylene

Figure 5 Tan δ *versus* temperature for a 9/1 (3K) sample: (a) cast from xylene; (b) annealed xylene sample
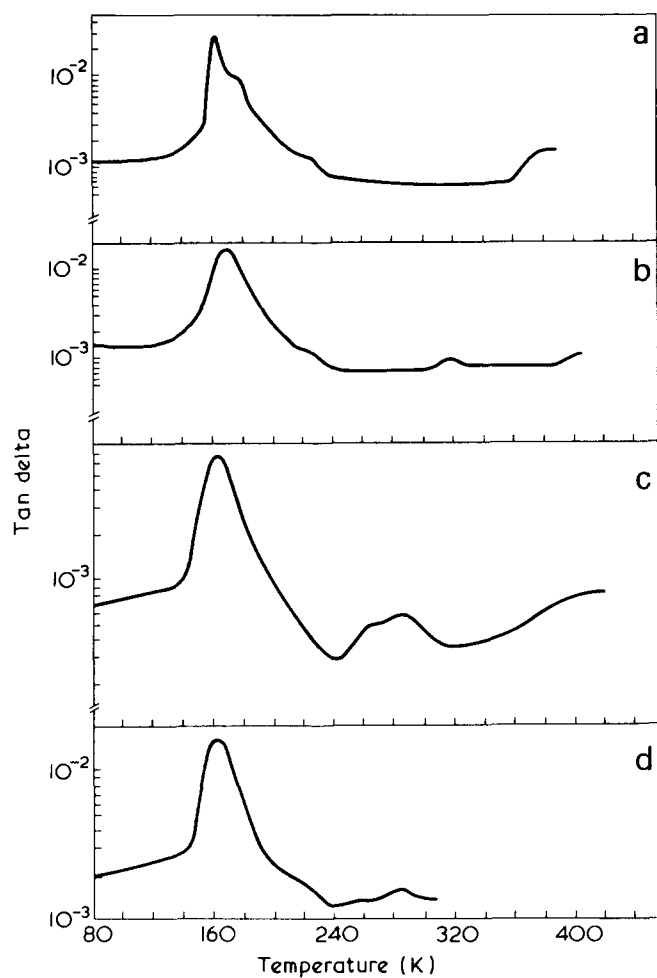
Figure 6 Tan δ *versus* temperature for a 9/1 (6.5K) sample: (a) cast from xylene; (b) annealed xylene sample; (c) cast from cyclohexane; (d) annealed cyclohexane sample

In the 6/4 case, the cyclohexane cast samples exhibit a broader relaxation peak than the samples cast from xylene at temperatures slightly higher than the T_g of PDMS (*Figures 3* and *4*). Each peak appears as a single relaxation skewed to the high temperature side of the maximum. Thermal annealing of the samples produces two overlapping relaxations with a narrow distribution peak at ~150K (the region of the PDMS T_g) and a second broad distribution peak at 180K.

In the case of the 9/1 samples, a series in which a molecular weight variation can be studied, the same effects are not observed in all samples. The 9/1 (3K) (*Figure 5*) exhibits properties similar to the 6/4 samples in that thermal cycling produces a double relaxation near the PDMS T_g. This effect is not observed to this extent with the 9/1 (6.5K) sample. The peak at 180K is shifted or removed with thermal annealing (*Figures 6a* and *6b*). For 9/1 (6.5K) cast from cyclohexane, thermal cycling narrows the distribution, changes the intensity and shifts the relaxation to slightly lower temperature (*Figures 6c* and *6d*). Thermal cycling of the xylene cast 9/1 (11K) and 9/1 (22K) samples (*Figures 7* and *8*) results in only slight changes such as the appearance of a small sharp peak in the 9/1 (11K) system.

No evidence is found in the dielectric spectra of the 6/4 polymers for the existence of PDMS crystals. In the 9/1 polymers small peaks near 200K may be due to motion during the crystal melt. These results are unlike the dynamic

mechanical data of Noshay and Matzner for polystyrene/ PDMS block copolymers in which the PDMS crystalline melt was observed at ~200K[23]. However, these results are similar to the dynamic mechanical and dielectric results of Kaniskin[8] for block copolymers containing PDMS and bisphenol-A polycarbonate in which the PDMS crystalline melt was not observed. These results indicate that some block copolymer morphologies created from either preferential or mutual solvents and from different sample thermal histories affect the extent of PDMS crystallinity.

If all samples are considered, two important general effects are noted as a function of thermal treatment: (1) an initial broad relaxation occurs at 160K; (2) upon thermal annealing of each sample except 9/1 (6.5K) this distribution changes to two relaxations; a narrow relaxation near 155K and a broad relaxation centred near 180K [6/4 and 9/1 (3K)] or remains relatively unchanged [9/1 (11K); 9/1 (22K)]. The opposite effect was observed for the 9/1 (6.5K) sample. Upon selective solvent casting either the broad relaxation peaks are diminished [9/1 (6.5K)] or the distribution is shifted to lower temperature.

Comparison of TEM results with dielectric results

In general the dielectric results are consistent with the *TEM* results. As a function of thermal annealing and selective solvent casting, the *TEM* results and the dielectric results indicate better phase-separated morphologies. The only exception is the comparison of the 9/1 (6.5K) xylene cast sample with the data for the annealed sample. The *TEM* results indicate a better phase-separated morphology upon thermal annealing while the dielectric data indicate better mixing of the block components upon annealing (*Figures 6a* and *6b*).

Analysis of dielectric properties

Relaxation intensities and assignments. In order to analyse the above dielectric results the tan δ intensity of the individual components must be considered. The T_g of PDMS has been shown[24] to have a tan δ_{max} of ~4.5 x 10^{-2}. Tan δ_{max}
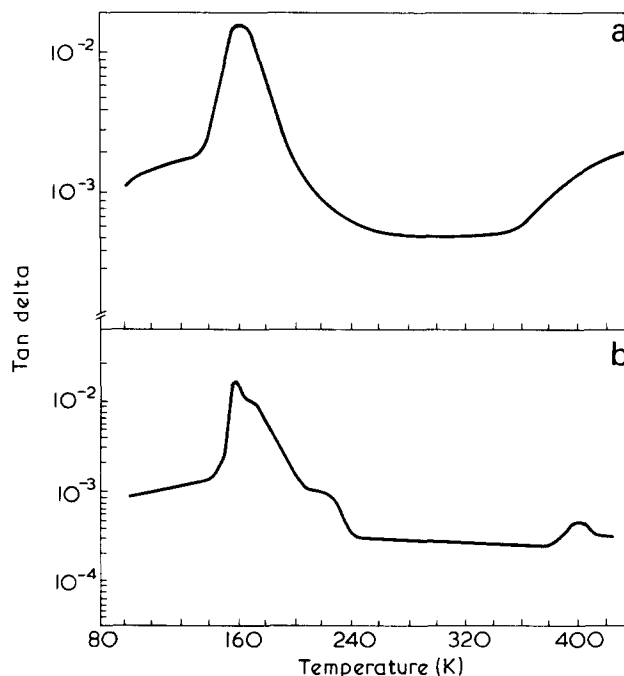

Figure 7 Tan δ *versus* temperature for a 9/1 (11K) sample: (a) cast from xylene; (b) annealed xylene sample

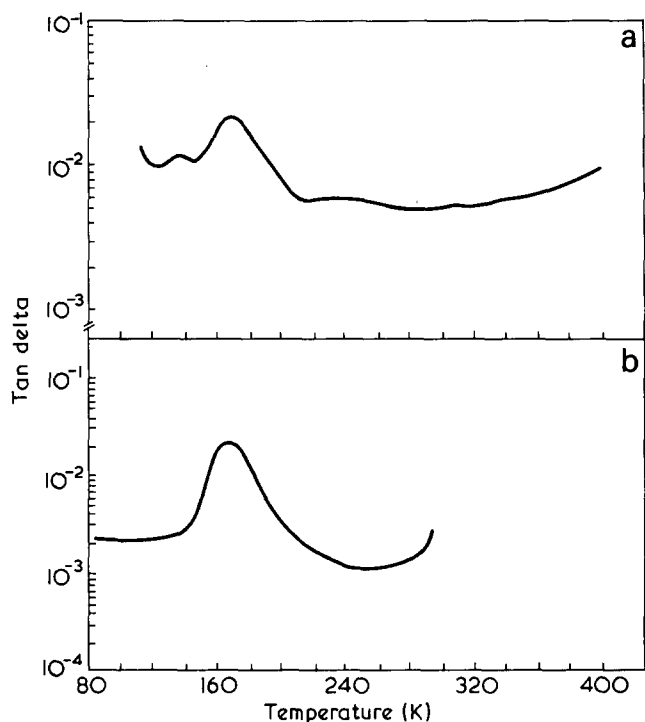*Figure 8* Tan δ *versus* temperature for a 9/1 (22K): (a) cast from xylene; (b) annealed xylene sample

of PαMS has been measured at 6.8×10^{-4} [25] as compared with 4×10^{-4} for polystyrene. The sub-T_g relaxations in styrene polymers exhibit tan δ_{max} an order of magnitude lower than those at T_g [27]. In the 9/1 spectra, the relaxations produced by the pure PDMS would be expected to be approximately two orders of magnitude stronger than those of PαMS. In the 6/4 case this ratio would be at least one order of magnitude. Because of these ratios, it must be concluded that the relaxations observed in the 9/1 case were due to pure PDMS, or to perturbed PDMS relaxations. In the 6/4 case (*Figure 4*) both polymer T_gs are observed; however, any relaxations below T_g of PαMS would most likely be due to PDMS. In both cases the observed relaxation spectra are due to (1) a single relaxation peak or (2) two relaxation peaks consisting of an almost pure PDMS phase and a mixed PDMS/PαMS phase at higher temperature. Temperature shifts toward the PDMS T_g and reduction of the tan δ of the higher temperature mixed phase are indicative of phase separation.

Correlation of critical molecular weight with dielectric results

As indicated previously, thermally annealed 6/4 and 9/1 (3K) materials exhibit two distinct dielectric relaxation peaks. One corresponds to the T_g for pure PDMS. The other is a wide distribution relaxation at ~180K. The 9/1 materials with PαMS molecular weights >6.5K exhibit only slight changes and a single broad relaxation peak after thermal cycling.

The critical molecular weight ($\bar{M}_c$) occurs at the break in the logarithmic relationship between molecular weight ($\bar{M}_w$) and melt viscosity (η) for homopolymers (1)[28,29].

$$\log \eta = A \log \bar{M}_w + B \qquad (1)$$

The constants A and B are dependent upon molecular weight. The value of A is 3.4 above the $\bar{M}_c$ of the polymer and ~1 below the $\bar{M}_c$ of the polymer. The $\bar{M}_c$ of PDMS is 30 000

and that for PαMS is 40 000[30]. All the block copolymers in this paper contain PαMS segments with molecular weight ($\bar{M}_w$) lower than $\bar{M}_c$. The 6/4 and 9/1 (3K) samples contain PDMS segments with $\bar{M}_w$ lower than $\bar{M}_c$ (see *Table 1*). All other 9/1 samples have PDMS segments with $\bar{M}_w$ higher than $\bar{M}_c$. For examples with PDMS $\bar{M}_w < \bar{M}_c$, interpolymer chain interactions and melt viscosity are low. Thermally stimulated demixing of the solvent generated phases occur and an almost pure PDMS phase is observed. For samples with PDMS $\bar{M}_w > \bar{M}_c$, intermolecular chain interactions and melt viscosity are high. Phase separation is hindered and essentially a single mixed phase is produced upon thermal cycling.

Therefore, within the 9/1 block copolymer series there are at least two competing factors for phase separation: (1) as the segment $\bar{M}_w$ is increased, the potential for phase separation is increased[18,19]; (2) as melt viscosity increases the block copolymer responds less readily to the thermodynamic conditions within the time-frame for annealing. For the 9/1 (3K) sample, essentially pure PDMS phases occur because of few interpolymer chain interactions and low melt viscosity. For the 9/1 (22K) sample, essentially pure PDMS phases occur less readily due to high melt viscosity. For 9/1 samples with intermediate segment molecular weights, it is difficult to predict the relative influences of these factors. Apparently for the 9/1 (6.5K) sample, essentially pure PDMS phases are not thermally generated because the driving force due to segment molecular weight is too low to overcome its high melt viscosity.

Most probable compositions of block segments within mixed phases

An estimate of the most probable compositions corresponding to the observed dielectric relaxations can be made using a mixing equation. Because of the arguments cited earlier, the observed peaks correspond to PDMS or mixed PDMS/PαMS phases. Although not strictly valid, we can assume a linear equation relating T_g to the weight components in the mixed phase:

$$CT_g(\text{PDMS}) + (1 - C)T_g(\text{PαMS}) = T_g \text{ meas} \qquad (2)$$

where C is the weight fraction PDMS in the mixed phase and the pure component T_gs are ~155K for PDMS and ~418K for PαMS. For samples containing PDMS with $\bar{M}_w > \bar{M}_c$, the most probable peak maximum is at 160K or slightly higher, corresponding to 98% PDMS. For the samples containing PDMS with $M_w < M_c$ [9/1 (3K) and 6/4 samples], a peak occurs at 180K; 90% PDMS. These estimated values indicate that the materials containing PDMS with $\bar{M}_w < \bar{M}_c$ have smaller amounts of PDMS in the mixed phase and are able to phase separate more efficiently than the samples having PDMS segments with $\bar{M}_w > \bar{M}_c$.

CONCLUSION

The dielectric and morphological properties of a series of 9/1 poly(dimethyl siloxane)(PDMS)/poly(α-methylstyrene) (PαMS) block copolymers and a 6/4 PDMS/PαMS block copolymer have been determined as a function of solvent casting and thermal treatment. Morphologies, as determined via transmission electron microscopy, showed differences between films cast from a PDMS preferential solvent (cyclohexane) and cast from a mutual solvent (xylene). The morphologies could not be considered as solvent induced equili-

brium conformations of the copolymers since the samples were dried rapidly. The results are very similar to those for polystyrene/PDMS block copolymers[22]. As expected, samples cast from the preferential solvents exhibited a more well defined granular structure. With increasing sample molecular weight, a supramolecular structure developed. Thermal cycling of the samples ($T = 498K$) above the T_g of both components for 30 min decreased the superstructure granularity and promoted better phase-separated domain structures.

The *TEM* results indicate better phase separation as a function of thermal annealing and casting from a solvent preferential to PDMS. The dielectric results are consistent with this except that 9/1 (6.5K) shows greater mixing character for the thermally annealed sample. The dielectric results are interpreted in terms of a random or most probable distribution of mixed PDMS/PαMS states which changes to a phase-separated bimodal structure consisting of pure PDMS and a mixed PDMS/PαMS phase upon thermal annealing or preferential solvent casting. This change mainly occurs in block copolymers which contain PDMS segments with molecular weights less than the PDMS critical molecular weight (30 000). For PDMS segments with molecular weights greater than 30 000, thermal cycling has little effect on the molecular distributions. These results are discussed in terms of the kinetic effects associated with polymer melt viscosity and with mixing character of the two components. Thermal cycling of the samples containing PDMS with $\bar{M}_w < \bar{M}_c$ resulted in an essentially pure PDMS phase and a mixed phase whose composition is 90% PDMS. For the higher molecular weight materials ($\bar{M}_w > \bar{M}_c$), the most probable composition of the mixed phase is estimated to be ~98% PDMS. It is also apparent that the block copolymer morphology created from either preferential or mutual solvents inhibits crystallization kinetics of PDMS below the crystal melting point.

ACKNOWLEDGEMENT

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