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Photon Correlation Spectroscopy of Bulk Siloxane Polymers

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ABSTRACT: A remarkable effect on the time correlation function of polarized Rayleigh scattered light for bulk poly(phenylmethylsiloxane) and poly(dimethylsiloxane–phenylmethylsiloxane) has been measured by means of photon correlation spectroscopy. The observed characteristic time has a q^2 dependence, with q being the magnitude of the momentum transfer vector, and is not related to local side-group (or structural) motions which can sometimes be detected by using depolarized Rayleigh scattering. We show, for the first time to our knowledge, that low molecular weight polymers having slight differences in the polarizabilities because of structural variations can exhibit local concentration fluctuations. The corresponding characteristic-time distribution function represents a measure of polydispersity for the bulk polymer.

Introduction

In a previous work[1] we reported polarized Rayleigh–Brillouin spectra of poly(phenylmethylsiloxane) (polymer A) and poly(dimethylsiloxane–phenylmethylsiloxane) (copolymer B). We were able to obtain information dealing with the side group (phenyl ring) motion of those polymers. In the Rayleigh–Brillouin spectra we observed a remarkable, and yet unaccounted for, effect in terms of the polarized Rayleigh intensity, which exceeded the value caused by local structural relaxation processes and density fluctuations. In a one-component fluid system, the polarized Rayleigh scattering arises mainly from local density fluctuations while in a multicomponent fluid system local concentration fluctuations may dominate.

Study of slow structural motions in terms of polarized Rayleigh line width distributions by means of photon correlation spectroscopy has been reported for bulk polystyrene near the glass temperature, T_g.[2,3] The main features of the observed correlation function are the large deviation from single-exponential form and the similarity between polarized and depolarized correlation functions as well as agreement of the relaxation time with dielectric relaxation measurements.[3,4]

In this paper we show, for the first time to our knowledge, that another type of motion can be responsible for the excess Rayleigh intensity. We attribute the additional contribution as due to polymers with repeating units having different polarizabilities. For this purpose we have measured correlation functions of poly(phenylmethylsiloxane) (polymer A) well above T_g, of poly(dimethylsiloxane–phenylmethylsiloxane) (50% in phenylmethyl, copolymer B) in the temperature range −10 to 40 °C, and of poly(dimethylsiloxane–phenylmethylsiloxane) (10% in phenylmethyl, copolymer C) at 20 °C.

Experimental Section

Photon correlation spectra at different temperatures were taken at a scattering angle $\theta = 90°$, without refractive index matching fluid, using the apparatus at Bielefeld.[5] The measurements at 20 °C and at different scattering angles were performed with the light scattering spectrophotometer at Stony Brook.[6] The light source was an argon ion laser (Spectra Physics) operating at $\lambda_0 = 488.0$ nm and ~400 mW. Both the incident beam and the scattered light were polarized perpendicular (V) to the scattering plane. This geometry gives the so-called VV spectral component of the scattered light. The single-clipped photocount autocorrelation function was measured by means of a 96-channel Malvern correlator.

All three polymers were purchased from Petrarch Systems Inc. (Levittown, Pa.). Polymer A was almost pure poly(phenylmethylsiloxane), copolymer B was ~50% in dimethyl and 50% in phenylmethyl randomly distributed in the chain, and the copolymer C was ~90% in dimethyl and 10% in phenylmethyl. The molecular mass of all three polymers was a few thousand daltons (~3000 g/mol and quite polydisperse). The samples were filtered through 0.45-μm Millipore filters directly into dust-free light scattering cells (10-mm o.d.).

Table I
Refractive Index, Density, Viscosity, and Glass Transition Temperature of Polysiloxanes

	polymer A	copolymer B
n^a	$1.643 - 3.64 \times 10^{-4}T$	$1.596 - 3.47 \times 10^{-4}T$
ρ,[a] g·cm^{-3}	$1.315 - 7.2 \times 10^{-4}T$	$1.289 - 7.6 \times 10^{-4}T$
η_s,[a] cP	$\eta_s = 2.56 \times \exp[433/(T - 217)]$	$\eta_s = 0.914 \times \exp[654.5/(T - 168)]$
T_g, K	227	199

[a] T in K.

Auxiliary Measurements. We have also measured the refractive index n, the density ρ, and the viscosity η_s of polymer A and copolymer B (Table I). A Höppler (falling ball) viscometer was used in the temperature range −10 to 40 °C, corresponding to viscosities of 400–0.1 P. The fit of the viscosity data to a non-Arrhenius equation of the form $\eta_s = \eta_0 \exp[A/(T - T_0)]$, where T_0 is a temperature close to T_g as determined by the DTA apparatus, is shown in Figure 1.

Data Analysis

The measured single-clipped photocount autocorrelation function for a detector of finite effective photocathode has the form

$$G_k^{(2)}(\tau) = A(1 + b|g^{(1)}(\tau)|^2) \qquad (1)$$

where $g^{(1)}(\tau)$ is the normalized correlation function of the scattered electric field, k is the clipping level, A is the background, and b is an unknown parameter in the data-fitting procedure, depending mainly on the clipping level, the coherence area, and the delay time. τ $(=I\Delta\tau)$ is the delay time, with I and $\Delta\tau$ being the channel number and the increment delay time, respectively.

For a polydisperse sample $g^{(1)}(\tau)$ has the form

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma) \exp(-\Gamma\tau)\, \mathrm{d}\Gamma \qquad (2)$$

where $G(\Gamma)$ is the normalized distribution of decay rates. First, we analyzed our data by the cumulants method.[7] In this case information is available in terms of the average line width $\bar{\Gamma}$ and its variance $\mu_2/\bar{\Gamma}^2$, where

$$\bar{\Gamma} = \int G(\Gamma)\Gamma\, \mathrm{d}\Gamma \quad \text{and} \quad \mu_i = \int (\Gamma - \bar{\Gamma})^i G(\Gamma)\, \mathrm{d}\Gamma \qquad (3)$$

We computed these with the formula

$$\ln (Ab)^{1/2}|g^{(1)}(\tau)| = \ln (Ab)^{1/2} - \bar{\Gamma}\tau + (1/2!)\mu_2\tau^2 \qquad (4)$$

In our case, $\mu_2/\bar{\Gamma}^2$ was 0.25 and 0.45 for copolymer B and

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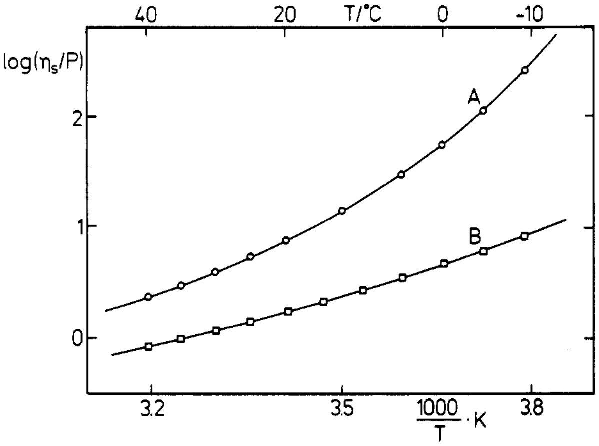

Figure 1. Shear viscosity of poly(phenylmethylsiloxane) (○) and poly(dimethylphenylmethylsiloxane) (□) as a function of temperature. The lines are the calculated fit to $\eta_s = \eta_0 \exp[A/(T - T_0)]$.

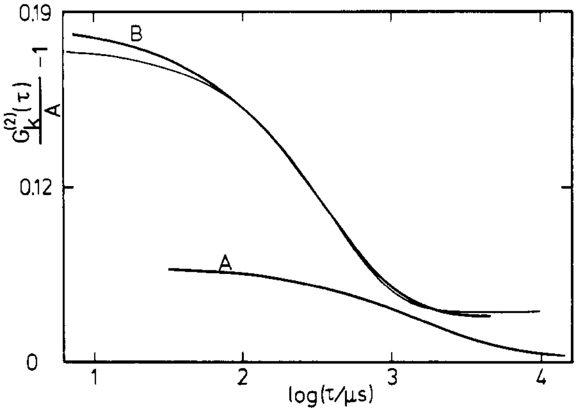

Figure 2. Correlation function $(G_k^{(2)}(\tau)/A) - 1$ for polymer A at 21.7 °C and copolymer B at 24.5 °C and $\theta = 90°$ with VV-scattering geometry. The thick lines are the fit to $a + b \exp[-2(t/\tau_0)^\beta]$. The 368 experimental points are located within the thickness of the fitted lines. The other line is the calculated fit to a single exponential ($\beta = 1$).

polymer A, respectively. On the other hand, we are interested in understanding the origin of the observed decay rates. In so doing, we have chosen the correlation function $g^{(1)}(\tau)$ to be of the empirical form[8]

$$g^{(1)}(\tau) = \exp(-t/\tau_0)^\beta \qquad (5)$$

where β ($0 < \beta \leq 1$) is a measure of the width of the distribution of decay times. The mean relaxation time $\langle\tau\rangle$ ($=1/\bar{\Gamma}$) is given by

$$\langle\tau\rangle = (\tau_0/\beta)\Gamma(\beta^{-1}) \qquad (6)$$

where $\Gamma(\beta^{-1})$ is the gamma function.

Figure 2 shows two typical correlation functions for polymer A and copolymer B, obtained by superimposing four successive measurements using different delay times $\Delta\tau$ (by a factor of 2 each time). For comparison we have plotted the fit to a single exponential ($\beta = 1$). We matched $G_k^{(2)}(\tau)/A - 1$ for each run by computing only a constant b. The combined correlation function has been fitted to the equation

$$(G_k^{(2)}(\tau)/A) - 1 = a + b \exp[-2(t/\tau_0)^\beta] \qquad (7)$$

where a accounts for a nonzero background.

Results and Discussion

Values of $\langle\tau\rangle$ as function of temperature for polymer A and copolymer B are listed in Table II. The mean relaxation time $\langle\tau\rangle$ is a decreasing function of temperature as shown in Figure 3 for the two bulk polymers A and B. By fitting the experimental data of Table II to a non-Arrhenius equation similar to the viscosity analysis for supercooled liquids, we obtained

$$\langle\tau\rangle_A = 2.6 \times 10^{-6} \exp[701.4/(T - 201)] \text{ for polymer A}$$
$$\langle\tau\rangle_B = 12.4 \times 10^{-6} \exp[469.4/(T - 189)] \text{ for polymer B} \qquad (8)$$

where $\langle\tau\rangle$ is expressed in seconds.

Table II
Mean Relaxation Time $\langle\tau\rangle$ and the Width of the Distribution β

polymer A		copolymer B	
T, °C	$\langle\tau\rangle$/ ms	T, °C	$\langle\tau\rangle$/ ms
-10	231	-6.4	5.3
-5	85	0.9	3.0
-0.1	39.8	9.9	1.9
8.7	16.9	24.5	0.93
15.3	8.6	39.3	0.55
21.7	4.9	$\beta = 0.83 \pm 0.01$	
31.2	2.1		
41.3	1.3		
$\beta = 0.79 \pm 0.02$			

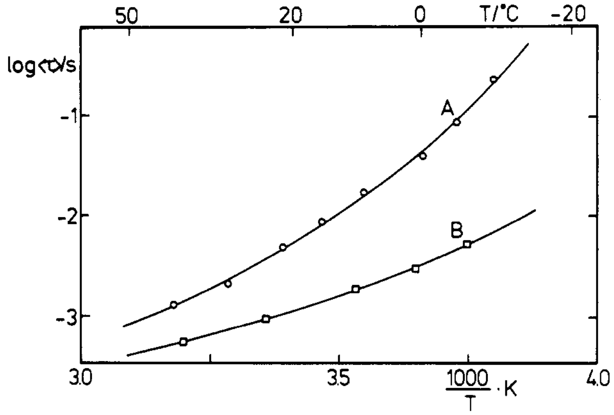

Figure 3. Mean relaxation time $\langle\tau\rangle$ (defined by eq 6) for polymer A and copolymer B fitted to $\langle\tau\rangle = \langle\tau\rangle_0 \exp[A/(T - T_0)]$.

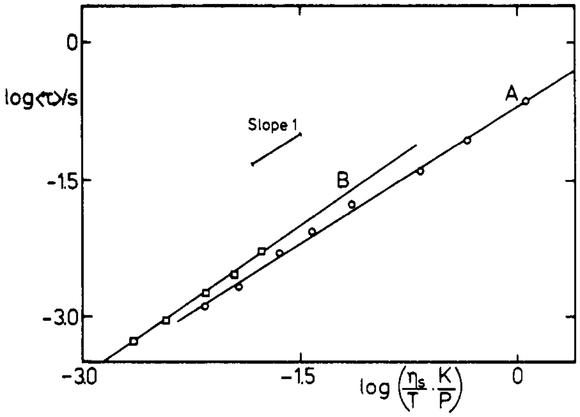

Figure 4. log-log plot of $\langle\tau\rangle$ vs. η_s/T.

The similarity on the temperature dependence between viscosity (Figure 1) and $\langle\tau\rangle$ is clearly demonstrated in Figure 4. This implies in some sense a diffusional character in the relaxation process. A map of the relaxation times for the polymers A and B, in addition to the dielectric relaxation for polymer A, is shown in Figure 5. A remarkable feature of this system as plotted in Figure 5 is the appearance of two distinct relaxation processes with

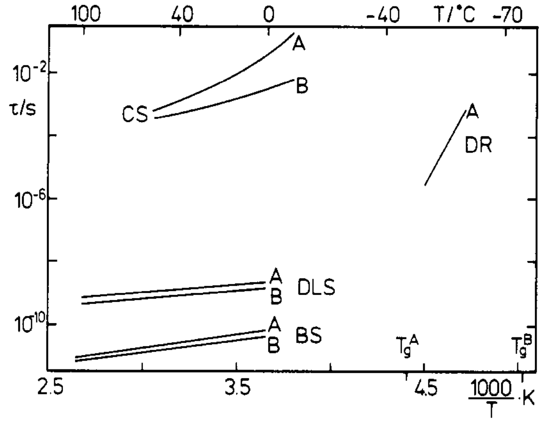

Figure 5. Temperature dependence of relaxation times of polymer A and copolymer B as probed by Brillouin scattering[1] (BS), depolarized light scattering[9] (DLS), correlation spectroscopy (CS), and dielectric relaxation (DR) (only for polymer A).

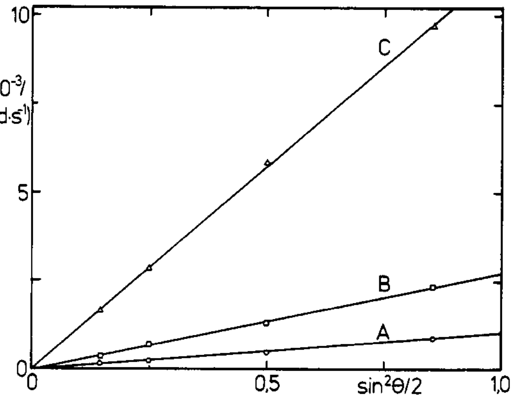

Figure 6. Plot of $\bar{\Gamma}$ vs. $\sin^2(\theta/2)$ at 20 °C for polymer A (○) and copolymers B (□) and C (△).

relaxation times differing by 8 orders of magnitude in both polymers. It is obvious from Figure 5 that the slow relaxation process which we have observed by photon correlation and the fast one followed by Fabry–Perot interferometry cannot be assigned to the same molecular motion. A comparison between the photon correlation results and the dielectric relaxation time leads to the same conclusion. Brillouin spectroscopy[1] (BS) and depolarized light scattering[9] (DLS) probe similar processes related to local side-group motions, while dielectric absorption[10] is caused by a different type of motion with much higher activation energy and it is more sensitive to the α mode (large-scale motions). In structural relaxations, the motions become very slow when approaching T_g from the high-temperature side. The polarized and the depolarized correlation functions as well as dielectric absorptions can be described by eq 5 using low values of β, usually, ~0.4. The $\langle\tau\rangle$ values obtained by these different methods are generally of the same order. None of these features seem to apply to the present case.

In order to identify the excess Rayleigh line width, we studied the q dependence [scattering vector $q = (4\pi n/\lambda_0)\sin(\theta/2)$] of the measured line width. The results at four scattering angles (45, 60, 90, and 135°) and 20 °C with $\lambda_0 = 488.0$ nm are shown in Figure 6. This quantitative picture points out clearly a diffusional character of the observed relaxation times. The puzzle remains: What kind of diffusional motion is possible to be seen with light scattering in bulk "one-component" polymers? For this purpose we measured the correlation function of copolymer C, which is 10% in phenylmethyl. The observed correlation function at 20 °C has a smaller contrast b and the line width scales again with q^2 (Figure 6). On the other hand, no correlation function could be resolved in the case of pure poly(dimethylsiloxane) ($M_w \sim 3900$) at 20 °C. It is worth mentioning that in the case of poly(dimethylsiloxane) the Landau–Platcek ratio ($I_R/2I_B$, with I_R and I_B being the Rayleigh and Brillouin line intensities respectively) is close to the classical (without relaxation) limit of $\gamma - 1$ ($\gamma = C_p/C_v$, the specific heat ratio). We have conjectured that the observed relaxation times can be assigned to "local concentration fluctuations" of the low molecular weight polymers having different molecular weights and polarizabilities. There could be a difference in the local refractive index between $Si(CH_3)(C_6H_5)$ and $Si(CH_3)_2$. The polysiloxane polymers contain low molecular weight oligomers which can be removed partially by heating the sample at ~200 °C under vacuum. We followed this procedure and found ~0.07% and 0.05% weight loss for polymer A and copolymer B, respectively. The correlation functions of the residues show the same dynamics as before. However, we did observe a reduced contrast b/A.

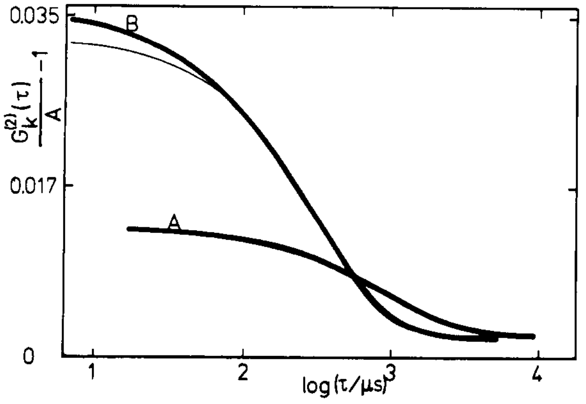

Figure 7. Correlation function $(G_k^{(2)}(\tau)/A) - 1$ for polymer A and copolymer B at 20 °C and $\theta = 90°$ with VV-scattering geometry. The two polymers were heat treated at 200 °C under vacuum. The thick lines are the fit to $a + b\exp[-2(t/\tau_0)^\beta]$. The 276 experimental points are within the thickness of the lines. The other line represents the single-exponential fit ($\beta = 1$).

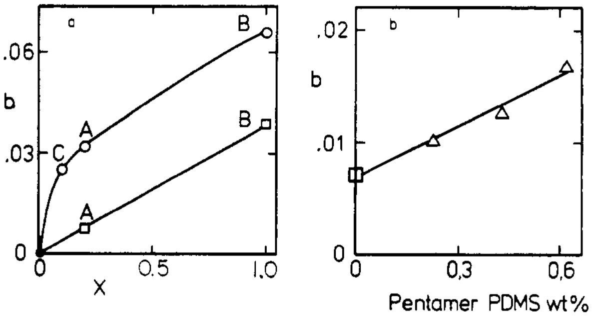

Figure 8. (a) The contrast b of the correlation function vs. the mole fraction of the repeating polymer units $X = 1 - [>Si(CH_3)_2]/[>Si(CH_3)(C_6H_5)]$. Symbols: ○) indicates samples A, B, and C without heat treatment; (□) denotes samples that had been heated under vacuum; (●) denotes poly(dimethylsiloxane) (PDMS). (b) The contrast b of the correlation function for polymer A vs. pentamer PDMS concentration in weight percent. The box denotes the same heat-treated polymer A as in Figure 8a.

Figure 7 shows these correlation functions for polymer A and copolymer B at 20 °C, $\theta = 90°$, and $\lambda_0 = 488.0$ nm. The reduction of the amplitude b, which is related to $(\delta n/\delta c)^2_{T,P}$ is demonstrated in Figure 8, where for comparison we have plotted b before treatment for the samples A–C. The x axis of this figure is a dimensionless parameter $X = 1 - |[>Si(CH_3)_2] - [>Si(CH_3)(C_6H_5)]|$, with [>Si-

$(CH_3)_2]$ and $[>Si(CH_3)(C_6H_5)]$ being the concentrations of these units in the polymer chain. The strength of the relation b to X is modulated by the polydispersity of the samples as suggested by the curvatures in Figure 8a.

A further test in the opposite direction was to examine the light scattering of polymer A (heating at 180 °C under vacuum) after addition of 0.22, 0.42, and 0.62 wt % of pentamer poly(dimethylsiloxane) (PDMS). The contrast b was increased by a factor of 2.3 for the highest pentamer PDMS concentration, while the change in the line width $\bar{\Gamma}$ was only 7%, which was mainly due to a slight decrease in the solution viscosity. This change in b upon addition of the pentamer PDMS is shown in Figure 8b. For this test we began with polymer A which had been heated under vacuum before (□).

We have observed local concentration fluctuations of bulk polysiloxane polymers and have attributed the spectra as small polarizability differences in the polymer repeating units. The time correlation function, then, becomes a measure which can be related to polydispersity of polysiloxane fluids and permits us to characterize such systems in a much more detailed manner by means of photon correlation spectroscopy.

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Small-Angle X-ray Diffraction Study of Thermal Transition in Styrene–Butadiene Block Copolymers

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ABSTRACT: The small-angle X-ray scattering technique is utilized to study the transition in styrene–butadiene block copolymers from a microdomain structure to a disordered homogeneous phase. The transition, occurring on raising the temperature, is reproducible and thermally reversible. The SAXS intensity pattern, exhibiting a main interdomain peak and a few secondary peaks at room temperature, shows a gradual decrease in intensity over a temperature range of more than 100 °C, but the position and the overall shape of the main peak remain unchanged. Analysis of the SAXS data shows that, with increasing temperature, the invariant and the length of inhomogeneity decrease, but the domain boundary thickness remains approximately constant. It is concluded that the disappearance of the microdomains proceeds by gradual intermixing of components into the opposite phases, with accompanying changes in the size of the microdomains, much in the same manner as would occur with coexisting phases of a binary liquid system. Even when the microdomains have finally disappeared and the mixture has become thermodynamically homogeneous, the SAXS pattern of diminished intensity persists, reflecting the presence of dynamic density inhomogeneity, as suggested in the theories of de Gennes and Leibler. The similarity of our SAXS results with those obtainable with a supercooled mixture undergoing a spinodal decomposition is pointed out and its thermodynamic basis discussed.

I. Introduction

Interesting and unique properties of block copolymers arise from the fact that they often attain geometrically regular arrangements of microdomains consisting of components segregated from each other. Electron micrographs revealing beautiful arrays of spheres, cylinders, and lamellae abound in the literature. The thermodynamic basis for such microdomain formation and the conditions leading to one or the other morphology have been enunciated by a number of workers[1-9] in the past decade.

On the basis of these theories and also of general thermodynamic considerations, one can expect that such microdomain structure becomes unstable under certain conditions and instead a homogeneous phase becomes a thermodynamically preferred one. Such a case will arise when the two components are very similar, when the block lengths are fairly short, when the temperature is raised or lowered (depending on whether the corresponding homopolymer pair exhibits a LCST or a UCST), or when a common solvent is added. It is of interest to know more about the characteristics of such a transition, for example the degree of abruptness of the change or the properties which exhibit discontinuity at the transition point. In practice such a transition may be encountered in some instances during processing of block copolymers at high temperatures. A transition phenomenon in general offers much more stringent tests of competing theories because assumptions which may otherwise be approximately valid can become severely strained at the transition region.

Chung and Gale[10] and Gouinlock and Porter[11] studied rheological properties of a styrene–butadiene triblock copolymer sample and found a discontinuity in its dynamic viscosity within a fairly narrow temperature range, which was attributed to disappearance of microdomain structure. Williams and others[12] made light scattering studies on a number of styrene–butadiene block copolymers to detect the transition on temperature change. The results were, however, somewhat inconclusive because of the experimental difficulty owing to the small size of the domains in comparison to the wavelength of light. Ramos and Cohen[13] prepared block copolymers of isoprene and butadiene of fairly high molecular weights, which remain homogeneous down to their glass transition temperatures even though the corresponding homopolymer pair was not