resin blends followed by a rise in tan δ toward a (not reached) second peak. Dynamic viscoelastometry on the optically clear, inhomogeneous blends of copolymers J and K with PPO resin has not yet been done.

Conclusions

Statistical copolymers of styrene-*p*-chlorostyrene (M_w ~3 -4 × 10^5) having cumulative mole fraction styrene $\bar{N}_s \geq$ 0.347 form homogeneous, single-phase blends with PPO resin ($M_w = 3.72 \times 10^4$). Styrene-*p*-chlorostyrene copolymers having cumulative $\bar{N}_s \leq 0.320$ form heterogeneous blends with PPO resin. A copolymer having cumulative $\bar{N}_s$ = 0.334 also appears incompatible with PPO resin, but it is definitely a borderline case. In the five blend systems for which thermo-optical, differential scanning calorimetric, and dynamic viscoelastic data were all obtained, each distinguished the homogeneous or heterogeneous character of the blends examined by detecting respectively one or two transition temperatures. The detection methods applied, and the results observed, are indicated in Table II. The relative sensitivities of these analytical tests for mobility transitions in detecting single or multiple glass transitions require further examination. Blends of copolymers K, J, M, and N with PPO resin should serve well for such future studies.

An attempt to assess the variation of copolymer–PPO resin thermodynamic interaction parameters with copolymer composition will be made in a forthcoming paper in which copolymer average molecular weights are varied.

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Low Temperature Thermal Expansions and Relaxations in Polyethylene

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ABSTRACT: Thermal expansivities α for two linear and a branched polyethylene have been measured between 100°K and room temperature. Both α and the derivative dα/dT are reported as a function of temperature and the results compared with low frequency dynamic data. In the region corresponding to the dynamically observed γ loss, two distinct dilatometric relaxations are found in all three polymers. The results are compared with those obtained previously for Nylons 66 and 11. Similarities and differences in the γ region are discussed in terms of various local motions proposed. Two additional relaxation regions are detectable at about 180 to 195°K. Above *ca.* 200°K, only a steep rise in α is discernible for both linear species, whereas the branched polymer exhibits stepwise increments.

In recent years we have extensively investigated the thermal expansivities of polymers at low temperatures in the amorphous[1] and in the semicrystalline state.[2] Accurate dilatometry has been demonstrated to be a successful low frequency method in dynamic mechanical investigations and, by virtue of the low effective frequency (10^{-3}–10^{-4} Hz), to resolve adjacent relaxation regions, where other methods may not indicate more than a shoulder in the plot of loss modulus *vs.* temperature.[1]

In this context polyethylenes are of particular interest, due to their simple structure, relatively high cyrstallinity, and the resulting controversies in the interpretation of their relaxation spectra. Thermal expansivities of a low density polyethylene and its copolymers with propylene have been reported.[2a] Volumes or lengths as a function of temperature have been measured by several authors.[3-5] They either give the volume–temperature results or their derivatives, using large temperature intervals. This makes it difficult at best to detect possible fine structures in the relaxation spectrum.

The purpose of this paper is to present dilatometric results for two linear and a branched polyethylene in the temperature range of 100–300°K, comparisons with two nylons, and tentative interpretations. Instrumentation and procedures have been previously described.[1c]

I. Materials and Experimental

The National Bureau of Standards' linear polyethylene (LPE), SRM 1475, and branched polyethylene (BPE), SRM 1476, were employed. To these was added the high molecular weight linear polymer (HMLPE), manufactured by and obtained from Allied Chemical Co. Characteristics of the three polymers are summarized in Table I. The melting points were determined by Olabisi.[6] Samples were compression molded into thin sheets (15–25 mils) at 30°K above their respective T_m's. Strips of 1.5 in. × 0.5 in. × 0.02 in. were cut from the molded sheet and then mounted on the double Dewar dilatometer. Cooling from room temperature to *ca.* 100°K was accomplished by filling the outer Dewar with liquid nitrogen. The inner one was filled with helium gas to promote heat transfer. The temperature of the copper block where the specimen resides was gradually raised at a constant heating rate of 0.5°/min. Length and temperature readings were recorded at 1° intervals. Linear

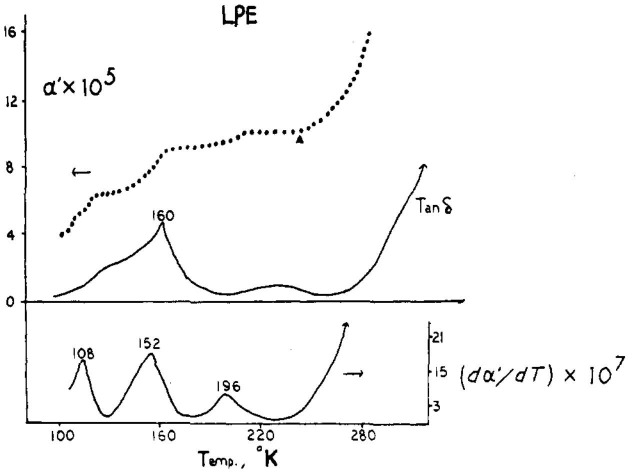


Figure 1. Linear thermal expansivity, α', temperature coefficient, $d\alpha'/dT$, and loss tangent[3] as a function of temperature for linear polyethylene. Triangle marks onset of sharp rise in α'.

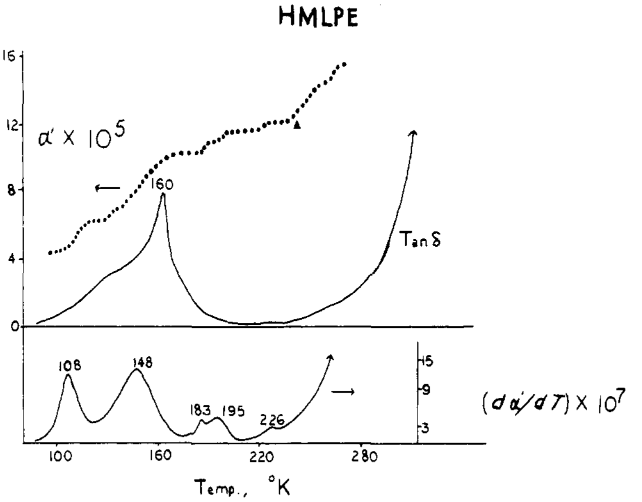


Figure 2. Linear thermal expansivity, α', temperature coefficient, $d\alpha'/dT$, and loss tangent[3] as a function of temperature for high molecular weight linear polyethylene. Triangle marks onset of sharp rise in α'.

thermal expansion coefficients $\alpha' = (1/l)(dl/dT)$ and the derivatives $d\alpha'/dT$ were calculated using a least-square moving-arc technique.[1c,2a] The dilatometer was calibrated against oxygen-free high-conductance copper.[1c,7,8]

Previous work has amply demonstrated the reliability of the instrumentation and method to be employed here for amorphous[1c] as well as semicrystalline[2c] systems. The precision of α' is $\pm 0.1 \times 10^{-5}$/°K. Hence only changes in α' exceeding 0.3×10^{-5}/°K will be considered significant.

II. Results

The quantities α' and $d\alpha'/dT$ as a function of temperature are shown in Figures 1–3 for the three polymers. Included are also the dynamic loss measurements reported in the literature.[3,9] We note in all instances a rapid increase of α' immediately following a characteristic near plateau region, which indicates the onset of the β relaxation and is marked by solid triangles.

It is not surprising to observe a two-step increase in α' at *ca.* 108 and 150°K for all three systems, although less pronounced and slightly displaced in BPE. Several experimenters have claimed on the basis of dynamic data the existence of unresolved or barely resolved multiple loss peaks in this temperature region[3,9–13] and have referred to a γ_{II} (low temperature) and a γ_I relaxation. The γ process is resolved here into two unambiguously separated peaks. The two steps in $\alpha'(T)$, which correspond to the two peaks in $d\alpha'/dT$, are denoted as T_{II} (low temperature) and T_I. The process is more pronounced in LPE and HMLPE. There α' increases by about 120 and 150%, respectively, in contrast with 50% in BPE. This despite the fact that BPE and HMLPE have similar degrees of crystallinity and densities (see Table I). In the temperature range between the γ and β regions, *i.e.*, between 160 and 220°K, we observe a step in $\alpha'(T)$ at 196°K (denoted as T_4) for LPE and a similar step in HMLPE, which might be resolvable into two closely adjacent peaks in $d\alpha'/dT$ at T_3 = 183 and T_4 = 195°K (see Figure 2). The BPE analysis, Figure 3, suggests two such peaks at T_3 = 178 and 203°K. The latter should for consistency be included in the β region because it is located above the characteristic temperature represented by the solid triangle. Above 200°K, BPE exhibits three steps at 203, 233, and 254°K, whereas HMLPE shows at best a very small one at 226°K, barely above the background, and in LPE only a monotonic increase is visible. The characteristic point is located at about the same temperature for the two linear species but is shifted by about 30° in BPE, compare Figures 1–3.

Table I
Characteristics of Samples Studied

	Crystallinity by X-ray	T_m,[a] °K	Density, g/cm^3	M_v	Source
LPE	0.75	403	0.9794	5.25×10^4	NBS, SRM 1475
HMLPE	0.55	403	0.9268	$>5.0 \times 10^6$	Allied Chem. Co.
BPE	0.50	386	0.9183	Unspecified	NBS, SRM 1476

[a] Reference 6.

III. Discussion

***T_I* and *T_{II}*.** Clearly, the two relaxation processes at about 108 and 150°K are related to the dynamic γ loss. From the values of T_I and T_{II}, and the effective frequency of the dilatometric experiment (*ca.* $10^{-3.8}$ Hz),[1c] combined with Illers' lowest frequency result,[9] the activation energies for processes I and II are estimated to 7 and 12 kcal/mol. This may be compared with 7 and 15 kcal/mol obtained by Illers from dynamic data solely.[9]

As for a molecular mechanism of the γ process, local motions of three to five methylene units have been suggested.[9,14] Recently Boyd and Breitling[15] (B–B) undertook a computer simulation study of a conformational change in an ethylene sequence from TGT to TG'T, see Figure 4C. They show for the transition paths considered that this process encounters two energy barriers. Their specific parameter assignments yield numerical values which happen to be close to those discussed above for the T_{II} and T_I processes, namely 7 and 11 kcal/mol. We recall also the crankshaft models for polyethylene proposed by Schatzki[16] and Boyer,[17] see Figures 4A and 4B. However, Olf and Peterlin[18] have pointed out that the former is not favored on statistical grounds, whereas the latter is energetically unfavorable. The B–B model, on the other hand, allows for a more extended conformation and hence is energetically more favorable. We remark that it would also be qualitatively consistent with the observation of a γ loss in Nylon 2 (polyglycine I)[19] and 1,1-disubtituted polyolefins.[20]

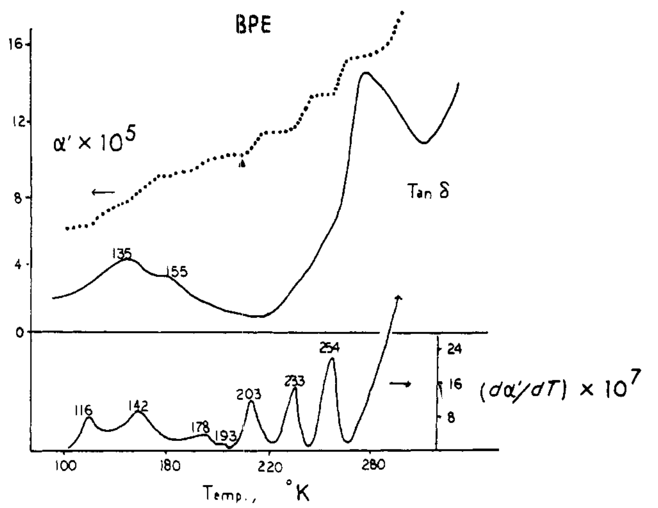


Figure 3. Linear thermal expansivity, α', temperature coefficient, $d\alpha'/dT$, and loss tangent[9] as a function of temperature for branched polyethylene. Triangle marks onset of sharp rise in α'.

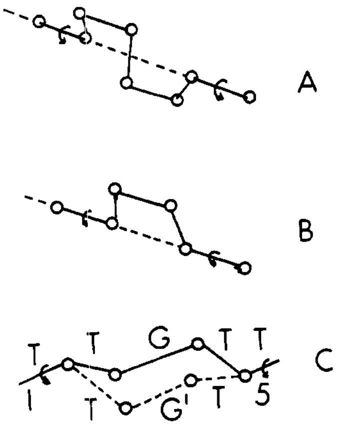


Figure 4. Various crankshaft type motions: (A) Schatzki;[16] (B) Boyer;[17] (C) Boyd-Breitling.[15]

We notice that the $T_{\rm II}$ and $T_{\rm I}$ relaxations have about equal strength, as judged by the peak values of $d\alpha'/dT$ in Figures 1–3. This is consistent with B–B, because the population of segments undergoing the $\gamma_{\rm II}$ transition equals that for the $\gamma_{\rm I}$ process provided the conformational change from TGT to TG′T is completed. If, due to some structural constraint, for instance, a methylene sequence in a fold or a surrounding matrix strained by sample deformation, the G to G′ transition cannot proceed as usual, we might see only a partial rotation, *i.e.*, a $\gamma_{\rm II}$ process. Indeed, in single crystals[21] or deformed linear polyethylene,[22] this is the only contribution observed.

In this connection it is of interest to compare polyethylene with nylons. In Figures 5 and 6, the corresponding results for Nylons 11 and 66 are exhibited.[2c,8] Once more the process can be separated into two peaks in the spectrum of $d\alpha'/dT$, with temperatures similar to those in polyethylene. However, there is *a significant* difference, since the peak heights are unequal in both nylons. The peak height ratio of $T_{\rm I}$ to $T_{\rm II}$ is unity for polyethylenes, whereas it is 0.5 for Nylon 11 and 4 for Nylon 66. The departure of this ratio from unity is ascribed to the presence of the amide groups. The difference in the ratio between Nylons 66 and 11 we believe is due to the mutual orientation of the amide groups. These two points are elaborated in what follows.

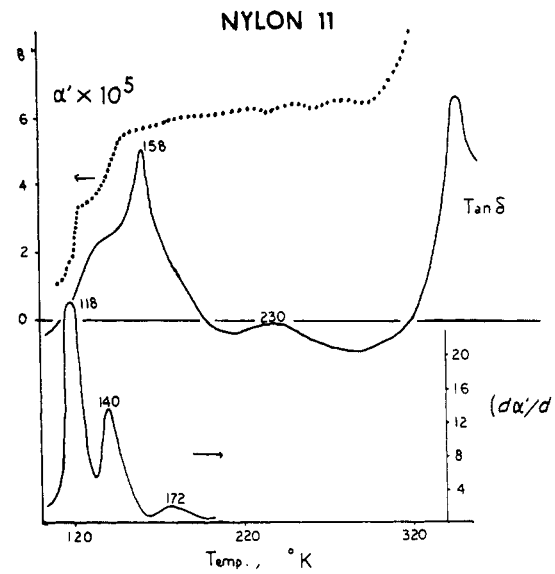


Figure 5. Linear thermal expansivity, α', temperature coefficient, $d\alpha'/dT$, and loss tangent as a function of temperature for Nylon 11.[23]

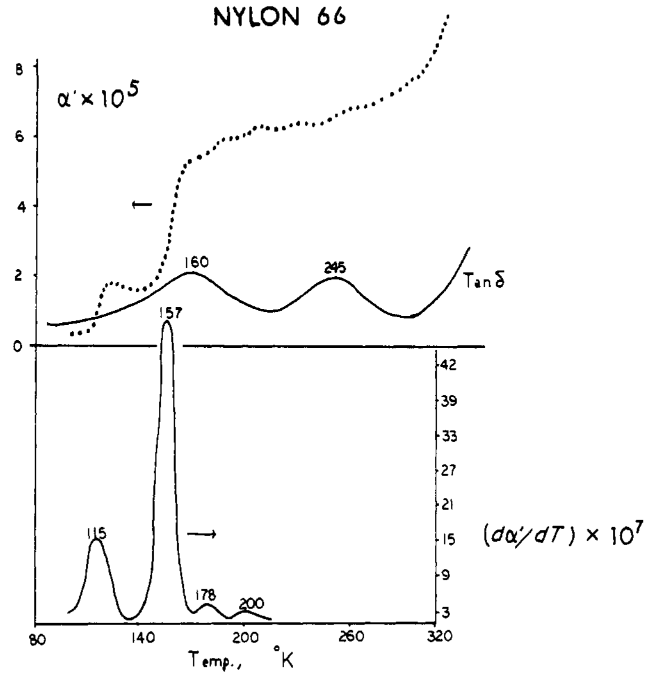


Figure 6. Linear thermal expansivity, α', temperature coefficient, $d\alpha'/dT$, and loss tangent as a function of temperature for Nylon 66.[23]

The γ process in nylon has been found to increase in intensity with increasing methylene length[23] and since it is associated with a pronounced dielectric loss, the amide group must be involved in the motion.[24] The transition from TGT to TG′T for the polyamide should develop as in polyethylene if only the methylene sequence is to be responsible. However, if the N–C_β or C–C_α bonds (*cf.*, Figure 7) have the gauche conformation in the sequence TGT, the B–B type of motion requires the amide plane to rotate. The path of this transition is different from that in the methylene sequence, and hence the relative intensity of $T_{\rm I}$ to $T_{\rm II}$ should also be different. Moreover, the bond rotation involving either of the above groups will sweep a larger volume than a C–C, and consequently the intensity of the γ process is greater than in polyethylene. The reversal of the intensity ratio may be understood in the following manner. For Nylon 66, the planar zigzag conformation shown in Figure 7 requires two consecutive amide groups to point in op-

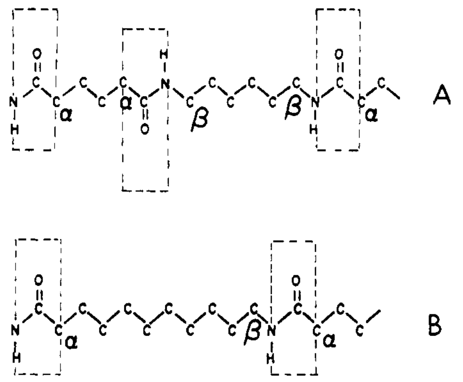
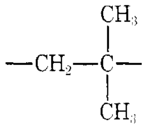


Figure 7. Nylon 66 (A) and Nylon 11 (B) in planar zigzag conformation. Amide planes shown by dashed lines. For explanation see text.

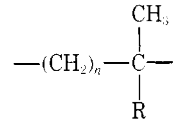
posite directions, whereas they are disposed in the same direction in Nylon 11. As suggested by B–B, the crankshaft motion can be visualized as the propagation of a kink (G or G′). Assuming this kink propagates through the nylon backbone, the sequences to be traversed are in Nylon 11 $-C_{\alpha}-(CH_2)_8-C_{\beta}-$amide–, whereas in Nylon 66 we have $-C_{\alpha}-(CH_2)_2-C_{\alpha}-$amide-$C_{\beta}-(CH_2)_4-C_{\beta}-$amide–. The inversion in the $T_{\rm I}$–$T_{\rm II}$ ratio may be related to the reversal from $\alpha\beta\alpha\beta$ to $\alpha\beta\beta\alpha$.

Consider finally the respective absence and presence of a γ loss in



$$-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-$$

and in



$$-(CH_2)_n-\overset{\displaystyle CH_3}{\underset{\displaystyle R}{C}}-$$

$n \geq 2$, R = CH_3 or C_2H_5, as observed by Hiltner, *et al.*[20] Since only two backbone atoms actually move in the B–B model, the crankshaft motion is still possible in the second compound.

In summary then: (1) the double γ process observed in polyethylenes and polyamides; (2) the differences in the intensity ratios of the two subprocesses; (3) the activation energies for this doublet process obtained by dilatometry and by dynamic measurements;[9] (4) the γ process in 1,1-disubstituted polyolefins,[20] lend strong support to B–B's proposal.

Very recently, Illers[9] (1974) has compared DSC scans on a branched and a linear polyethylene, which appear to be similar to our BPE and HMLPE. Whereas the former exhibits no step, a single step extending from about 150 to 165°K is observed in the latter. We have no explanation to offer for this difference between the results of the two methods. However, we observe the considerably higher scanning rate, 10 *vs.* our 0.5°C/min. Also, note again the considerably lower dilatometric step heights and peaks in the γ region of BPE. In this connection it should be recalled that in several amorphous polymers subglass relaxations are apparent in the thermal expansivity, when the heat capacity reveals only the main glass transition. This may result from experimental factors and/or the fact that the measured heat capacity contains both internal and configurational contributions (with the latter being the smaller fraction), whereas the thermal expansivity is a purely configurational property.

Whereas the peak height in tan δ is inversely related to the crystalline content, a direct relationship is observed in the dilatometric experiment, see Figures 1–3. Thus it appears that the configurational change accompanying the release of the motion in the volume experiment is larger in the more crystalline system and this may be indicative of an entropy effect. To be sure, a temperature-dependent contribution to $d\alpha'/dT$ by the crystalline fraction is included. However, above 100°K, this must be small.

T_3 and T_4. The characteristic temperature T_4 located at 196 and 195°K for the two linear species, *cf.* Figures 1 and 2, appears to be independent of crystallinity. In BPE no significant peak around these temperatures is noticeable. Several investigators[25-27] have claimed 195 ± 10°K as the main glass transition temperature, based on copolymer extrapolations. The observed constancy of T_4, at least between 55 and 75% crystallinity, would not be inconsistent with such an assignment.

The temperature T_3 decreases with decreasing crystallinity, being 183 and 178°K for HMLPE and BPE, respectively, and represents a borderline situation. It is not seen in LPE.

$T > T_4$. Above T_4, the α's of LPE and HMLPE increase monotonically with temperature, although there is some evidence of a small step in HMLPE at 226°K. The low density BPE, on the other hand, exhibits a stepwise increase with three relaxations located at 203, 233, and 254°K. In this temperature range measurements of thermal depolarization current[28] indicate four peaks (216, 221, 268, 300°K) for BPE and five (217, 233, 255, 263, and 273°K) for LPE. Zakin, *et al.*,[2a] observe for a low density polymer dilatometric transitions at 210, 250, and 270°K in addition to γ. The origin of these relaxations is not clear.

We locate the solid triangles in Figures 1–3 at about 240, 230, and 200°K for LPE, HMLPE, and BPE, respectively. Thus this significant difference between the linear and branched species may reflect a difference in the nature rather than the gross extent of crystallinity. This question remains to be pursued.

The rapid increase of α' in linear polyethylenes LPE and HMLPE obliterates any fine structure. It may be associated with the very strong relaxation at *ca.* 235°K observed by the group of workers at the National Bureau of Standards by means of thermal drift[29] and time effects.[4] It is interesting to note that in contrast to those and our results, the corresponding mechanical β-loss activity is quite small, sometimes even undiscernible.[3,9,12] This relaxation may be related to Boyer's upper glass transition temperature $T_g(U)$.[27] If so, one may ascribe the T_4 process which is independent of crystalline content to $T_g(L)$.[27]

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Small Angle Light Scattering by Elastomer-Reinforced Epoxy Resins

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ABSTRACT: Thermoset epoxy resins can be toughened by means of small elastomeric inclusions. A carboxyl terminated butadiene–acrylonitrile random copolymer (CTBN) was dissolved in a mixture of cycloaliphatic resin with its hardener. The elastomer precipitates during polymerization and small domains of a few microns in size can be viewed in thin sections of the solid polymer after staining with OsO_4. The variation in size and shape of the spherical domains was studied as a function of CTBN content by small angle light scattering and the derived parameters were compared with those obtained *via* transmission electron microscopy. For CTBN concentrations less than 20%, spherical rubber inclusions about 4 μ in size were found by light scattering. Beyond 20%, epoxidic domains are present of about the same size. The morphological changes occurring during polymerization were followed continuously by means of light scattering. It was found that phase separation takes place well before the gelation point and occurs in a time interval which is nearly independent of CTBN concentration. Static deformation of the samples was monitored by light scattering and change in the scattering envelope as a function of elongation was recorded. It was concluded that the spherical domains become ellipsoidal with a tendency toward correlated orientation in the direction of stretch.

Light scattering (LS) analysis of polymer systems is now a well-known tool for quantifying their solid-state morphology. Textural information at the level 0.1–50 μ can be obtained, depending upon the scattering range which is recorded. Two different approaches are available.

If the system has a well-defined superstructure which can be represented by rather simple models, one can use a simulation method. Starting from the amplitude scattered by each element, one draws a theoretical scattering pattern that can be compared to the experimental one for further refinement. This approach has successfully provided a semiquantitative characterization of partially crystalline textures such as spherulites,[1] collagen,[2] cellulose rods,[3,4] or even more complex helicoidal fibers.[5]

If the structure is poorly defined, *i.e.*, made of entities of complex shape or with a broad size distribution, a useful treatment is the correlation method originally proposed by Debye and Bueche.[6] This process relates the scattered intensity to fluctuations[7] of the dielectric constant (ϵ) inside the material. A correlation function $\gamma(r)$ can be derived from the intensity which correlates the fluctuations η_1 of ϵ at some arbitrary point 1 in the medium with η_2 at some other point 2, a distance r away.

$$\gamma(r) = \langle \eta_1 \eta_2 \rangle / \langle \eta^2 \rangle$$

$\langle \eta^2 \rangle$ = mean square fluctuations, $\langle \eta_1 \eta_2 \rangle$ = average overall possible locations of 1 and 2, r staying constant. The function $\gamma(r)$ is clearly 1 for $r = 0$ and tends toward 0 for large values of r. If $\gamma(r)$ decreases faster with r for one medium than for another, it means the former is more heterogeneous.

In principle $\gamma(r)$ can be extracted from the intensity data by Fourier inversion. In practice, it is difficult to derive an analytical expression for $\gamma(r)$ when a complex system is involved but it is often possible to fit an exponential $[\exp(-r/a)]$ or a Gaussian $[\exp-(r/a)^2]$ function to experimental curves of $\gamma(r)$ *vs.* r. Determination of the parameter a, which is qualitatively related to the size of the density fluctuations, is then straightforward.

Two more parameters can be defined: an average length of heterogeneity $l_c = 2\int_0^\infty \gamma(r)\,dr$, and a volume of heterogeneity $v_c = \int_0^\infty \gamma(r) 4\pi r^2\,dr$.

In this paper the scattering of polarized light by rubber-epoxy composites, acrylonitrile–butadiene–epoxy (ABE) network copolymers, will be discussed: in the solid state as a function of rubber concentration, under conditions where the sample is subjected to a static deformation, and during polymerization while phase separation occurs. Both simulation and correlation methods are used for data interpretation.

ABE Composites. The toughening of glassy thermoplastics by addition of small amounts of elastomers has been used for some time to prepare important commercial products such as high impact polystyrene or acrylonitrile–buta-