Therefore the entropy change of transition, from the compact to the extended coil form, of (MA–DSt)$_n$ may be more negative than that of (MA–St)$_n$ due to a more extensive hydration of (MA–DSt)$_n$ in the coil form. Also, the transition enthalpy ΔH_t° of (MA–DSt)$_n$ can be expected to be somewhat larger than that of (MA–St)$_n$, because the increase in size of the phenyl residue on deuteration results in weak van der Waals interactions in the compact form. Thus the compact form of the deuterated polymer is suggested to be more stable than that of the nondeuterated one.

The calorimetric ΔH_t° of (MA–DSt)$_n$ has not yet been determined, and the van't Hoff ΔH_t° ($=\Delta H_{\text{vH}}$) of (MA–St)$_n$ could not be accurately determined. Also, the cooperative parameter σ ($=(\Delta H_{\text{cal}}/\Delta H_{\text{vH}})^2$) for formation of the compact form in (MA–DSt)$_n$ has not yet been studied. Therefore, the values of ΔH_t° and ΔS_t° for the maleic acid copolymers cannot be compared here. In the future, the calorimetric ΔH_t° or the σ value of the transition of (MA–DSt)$_n$[12,30] should be determined so that comparisons of the ΔH_t° and ΔS_t° values for (MA–St)$_n$ and (MA–DSt)$_n$ may be made, which may lead to additional evidence indicating the importance of enhanced hydrophobicity due to deuteration of the phenyl groups in the maleic acid copolymer.

Although the conformational effects of deuteration of hydrogens in the hydrophobic polyelectrolytes have not yet been studied and discussed, stabilization of the compact form of (MA–St)$_n$ obtained here by deuteration of the phenyl groups may be concluded to be due to cooperative enhancement of the hydrophobic interaction between the phenyl groups.

Conclusions

A maleic acid–deuterated styrene copolymer in the compact form at acidic pH can change conformation to the extended coil form by ionization of the carboxyl groups in aqueous NaCl. The pH, optical, viscometric, and ^{1}H NMR titrations indicated behaviors very similar to that of a maleic acid–nondeuterated styrene copolymer. However, from the transition curve and the temperature dependence of the transition, the compact form of the deuterated copolymer was concluded to be more stable than that of the nondeuterated copolymer. Increase in size of the side chain in the maleic acid–styrene copolymer upon deuteration of the phenyl groups may enhance the hydrophobic hydration around the side chains and lead to a more stable compact conformation.

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References and Notes

(1) Mandel, M.; Leyte, J. C.; Stadhouder, M. G. *J. Phys. Chem.* **1967**, *71*, 603–612.
(2) Crescenzi, V. *Adv. Polym. Sci.* **1968**, *5*, 358–386.
(3) Crescenzi, V.; Quadrifolgio, F.; Delben, F. *J. Polym. Sci., Part A-2* **1972**, *10*, 357–368.
(4) Braud, C.; Muller, G.; Feno, J. C.; Sélègny, E. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2767–2778.
(5) Okamoto, E.; Wada, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2413–2422.
(6) Bottiglione, V.; Morcellet, M.; Loucheux, C. *Makromol. Chem.* **1980**, *181*, 469–484.
(7) Morcellet-Sauvage, J.; Morcellet, M.; Loucheux, C. *Makromol. Chem.* **1982**, *183*, 839–848.
(8) Fichtner, F.; Schonert, H. *Colloid Polym. Sci.* **1977**, *255*, 230–232.
(9) Joyce, D. E.; Kurucsev, T. *Polymer* **1981**, *22*, 415–417.
(10) Sugai, S.; Nitta, K.; Ohno, N.; Nakano, H. *Colloid Polym. Sci.* **1983**, *261*, 159–165.
(11) Dubin, P. L.; Strauss, U. P. *J. Phys. Chem.* **1970**, *74*, 2842–2847.
(12) Dubin, P. L.; Strauss, U. P. "Polyelectrolytes and Their Application"; Rembau, A., Sélègny, E., Eds.; Reidel: Dordrecht, 1975; pp 3–13.
(13) Strauss, U. P.; Vesnaver, G. *J. Phys. Chem.* **1975**, *79*, 1558–1561.
(14) Strauss, U. P.; Schlesinger, M. *J. Phys. Chem.* **1978**, *82*, 571–574.
(15) Martin, P. J.; Strauss, U. P. *Biophys. Chem.* **1980**, *11*, 397–402.
(16) Davenport, J. N.; Wright, P. V. *Polymer* **1980**, *21*, 287–292.
(17) Davenport, J. N.; Wright, P. V. *Polymer* **1980**, *21*, 293–302.
(18) Ohno, N.; Nitta, K.; Makino, S.; Sugai, S. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 413–425.
(19) Sugai, S.; Ohno, N.; Nitta, K. *Macromolecules* **1974**, *7*, 961–963.
(20) Okuda, T.; Ohno, N.; Nitta, K.; Sugai, S. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 749–755.
(21) Sugai, S.; Ohno, N. *Biophys. Chem.* **1980**, *11*, 387–395.
(22) Sugai, S.; Nitta, K.;f Ohno, N. *Polymer* **1982**, *23*, 238–242.
(23) Ohno, N. *Polym. J.* **1981**, *13*, 719–726.
(24) Ohno, N.; Sugai, S., unpublished.
(25) Stillinger, F. H. *J. Solution Chem.* **1973**, *2*, 141–158.
(26) Stillinger, F. H. *Science (Washington, D.C.)* **1980**, *209*, 451–457.
(27) Samoilov, O. Ya. *Zh. Fiz. Khim.* **1978**, *52*, 1857–1862.
(28) Dutta-Choudhury, M. K.; Miljevic, N.; Van Hook, W. A. *J. Phys. Chem.* **1982**, *86*, 1711–1721.
(29) Frank, F. "Water"; Frank, F., Ed.; Plenum Press: New York, 1975; Vol. 4, pp 1–94.
(30) Ohno, N.; Nitta, K.; Sugai, S. *J. Polym. Sci., Polym. Ed.* **1978**, *16*, 513–521.

Deuterium-Exchange Preparation for Small-Angle Neutron Scattering Samples of Saturated Polymers

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ABSTRACT: Deuterium–hydrogen exchange catalyzed by a suspended rhodium catalyst has been used to achieve partial deuteration of a saturated polymer, hydrogenated polybutadiene. IR and density measurements show that about 6% of the hydrogen is replaced by deuterium. Small-angle neutron scattering indicates an exchange of 60% of the hydrogens in 10% of the chains. No evidence of unwanted side reactions involving the carbon–carbon backbone of the chain was observed.

Introduction

Small-angle neutron scattering (SANS) experiments are performed on mixtures of deuterated and hydrogenated polymer chains to determine information such as single-chain conformation in the bulk state. One of the problems with these experiments is the inability to match exactly the labeled and unlabeled species in terms of molecular size and chemical microstructure. A matched set of deu-

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terated and hydrogenated chains is most helpful for interpreting SANS patterns from mixtures containing high concentrations (volume fraction $\phi \approx 0.5$) of either species.[1] Three possible methods of obtaining matched pairs are (1) saturation of a common parent polymer with different elements to obtain neutron scattering contrast (e.g., hydrogenated polybutadiene and deuterated polybutadiene made from the same polybutadiene[2]), (2) parallel synthesis of otherwise identical polymers from labeled and unlabeled monomers, and (3) chemical exchange of a labeling element to form a labeled (deuterated) polymer from an unlabeled (hydrogenated) one. The first method requires an unsaturated parent polymer. While this method has been successfully utilized in SANS experiments, it is not applicable to most polymer systems. The drawback to parallel synthesis is the precise control of reaction conditions and/or numerous polymerizations necessary to produce a matched pair of polymers. The third technique should be ideal for producing matched pairs of polymers, yet is has received very little attention to date. By replacement of hydrogen with deuterium in an exchange reaction, a labeled polymer can be synthesized from the conventional polymer in one simple step.

D–H exchange has been reported for the aromatic sites of polystyrene,[3] and the resulting polymers have been used for NMR studies of chain dynamics.[4-6] On the basis of successful D–H exchange with low molecular weight alkanes in the presence of heterogeneous catalysts.[7,8] we were encouraged to attempt a similar reaction with *saturated* polymers. We report here a partial D–H exchange accomplished on hydrogenated polybutadiene (HPB) with no evidence of side reactions modifying the chemical microstructure of the chains. HPB was selected for this initial experiment because we have considerable experience with molecular characterization and SANS of it and its partially deuterated analogues.[2,9,10] Furthermore, use of nearly monodisperse HPB eliminates any complication resulting from a possible molecular weight dependence of the reaction in this heterogeneously catalyzed system.

Experimental Section

HPB, a saturated polymer similar to polyethylene containing an average of 18 ethyl side branches per 1000 skeletal carbon atoms, was synthesized from polybutadiene as reported previously.[9] The molecular weight of the parent polybutadiene (PB) was 1.53×10^5 as determined from both light scattering in cyclohexane at 25 °C and intrinsic viscosity measured in tetrahydrofuran at 25 °C. The PB was nearly monodisperse ($M_w/M_n < 1.05$) as shown by gel permeation chromatography (Waters GPC, Model 200). It is important to note that there was no evidence for residual unsaturation in the HPB by IR spectroscopy. This means that the concentration of double bonds was less than 0.1% in the polymer subjected to exchange.

Deuterium labeling was done with a hydrogen–deuterium exchange reaction. The HPB was dissolved in cyclohexane (2 g/L) and subjected to 500 psi deuterium at 92 °C in the presence of a heterogeneous catalyst, 5% rhodium on charcoal (2 g/L). After 5 h of reaction time, the exchanged polymer D-HPB, was recovered by hot filtration and subsequent precipitation in cold methanol. Intrinsic viscosities were measured in trichlorobenzene solutions at 135 °C to ensure that the exchange reaction did not severely affect the size of the polymer chains. The results were $[\eta] = 2.07$ dL/g for the HPB and $[\eta] = 1.90$ dL/g for the exchanged D-HPB. These quantities are nearly the same, the difference being scarcely significant in view of the ±5% precision of our technique for measuring $[\eta]$ at high temperatures. A small (ca. 1%) decrease in $[\eta]$ is expected due to the higher density of the exchanged D-HPB molecules.

Evidence of D–H exchange was obtained by IR, density measurements, and SANS patterns. The IR spectra were recorded on a Perkin-Elmer 283 spectrometer. Densities of compression-molded, ice-water-quenched samples were determined in a gradient column of water and 2-propanol. SANS measurements were done on the undiluted exchanged sample (D-HPB) and on a $\phi' = 0.5$ blend of D-HPB with the unexchanged HPB. (ϕ' designates the volume fraction of D-HPB, as opposed to ϕ, the volume fraction of labeled molecules.) The exchanged sample were run on the 30-m facility at Oak Ridge National Laboratory with a sample–detector distance of 11 m. The blend was run on the 10-m facility with fixed sample–detector distance of 4.5 m. Both experiments used neutrons of wavelength $\lambda = 4.75$ Å. Corrections were done in the usual manner[9] to obtain azimuthally averaged profiles of the coherent intensity. These were converted to absolute differential cross sections by comparison to the scattering from an Al secondary standard.

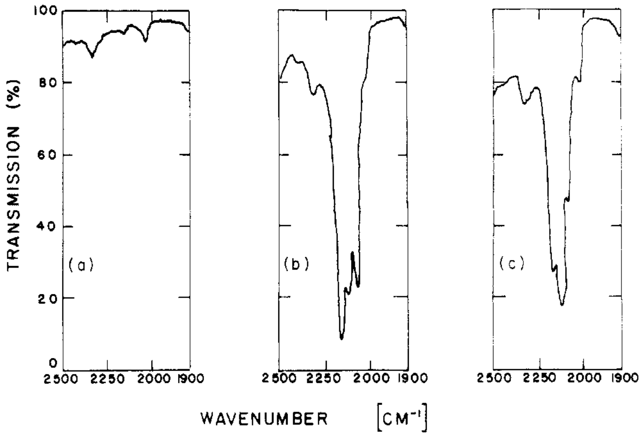

Figure 1. Infrared spectra for (a) HPB, (b) D-HPB, and (c) a $\phi = 0.1$ blend of DPB in HPB prepared from a common PB.

Results and Discussion

Qualitative evidence that D–H exchange has indeed taken place is seen from the IR spectra in Figure 1. There are shown the absorption spectra of the unexchanged HPB (curve 1a), the exchanged D-HPB (curve 1b), and a $\phi = 0.1$ blend of deuterated polybutadiene, DPB, in a matrix of HPB (curve 1c). The latter sample has been used in SANS studies reported previously.[9] Those polymers containing deuterium have three absorption maxima at $\nu \approx 2100$ cm^{-1}. The spectrum of perdeuteriopolyethylene, $(CD_2)_n$, not shown, does not have the central peak at $\nu = 2140$ cm^{-1}; that is presumably due to vibrations of the CDH moiety. Since we do not have a reliable absorption coefficient for this additional peak, IR intensities cannot be used to establish the concentration of deuterium in these partially deuterated samples. We have determined by separate means, however, that the fraction of deuterium in the DPB sample is $y = 0.4$.[9] As the intensities are similar for the undiluted exchange sample (Figure 1b) and the $\phi = 0.1$ blend of DPB (Figure 1c), we conclude that the exchange reaction described above led to replacement of ~5% of the hydrogens in HPB.

A similar quantity is obtained from measurements of the density increase resulting from the exchange reaction. We make the assumptions that deuteration conserves molar volume and further does not affect morphology (crystallinity). Then the densities of the unexchanged HPB ($\rho_H = 0.9026$ g/cm^3) and the exchanged D-HPB ($\rho_D = 0.9108$ g/cm^3) having identical quenched thermal histories can be used to determine the overall fraction of deuterium according to

$$\langle y \rangle = m_H(\rho_D - \rho_H)/8\rho_H \qquad (1)$$

where $m_H = 56.10$ is the magnitude of the formula weight of a C_4H_8 repeat in HPB. This procedure yields $\langle y \rangle = 0.065$, in good agreement with the semiquantitative IR results.

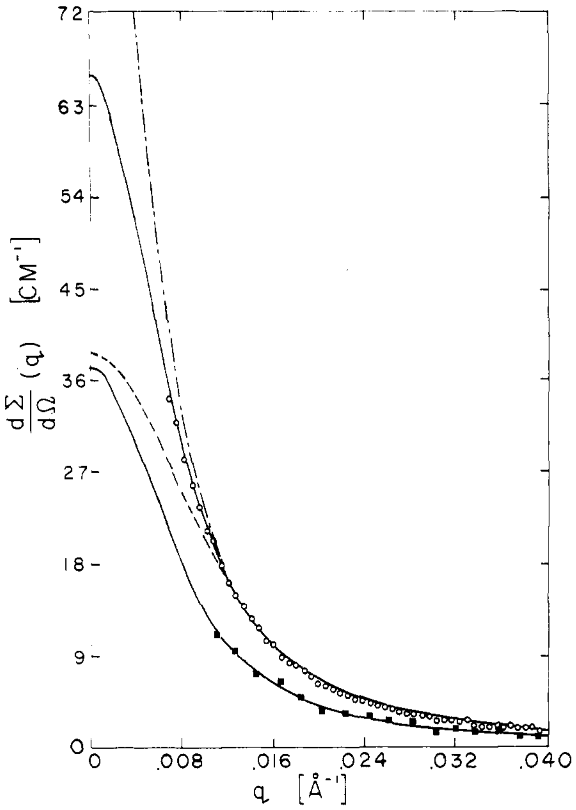

Figure 2. SANS scattering data for the unblended D-HPB (○) and the 50% D-HPB/HPB (■). The solid curves represent the best fits of eq 2 and 5 to the data. The broken curves are for R_g = 150 Å (– – –) and r_g = 280 Å (–·–), which are 30% deviations from the best-fit curve of 215 Å for the unblended sample.

Since both IR and density show that only a small fraction of the hydrogens were exchanged for deuterium, the question to be answered is how uniform is the exchange reaction? Were all chains exchanged by the same small amount, or are some chains reacted appreciably more than others? This can be answered by analysis of the SANS patterns, using the relation for the coherent cross section of an ideal molecular mixture of labeled and unlabeled chains[1,2]

$$\frac{d\Sigma}{d\Omega}(q) = KNP(q) \tag{2}$$

where N is the degree of polymerization, $P(q)$ is the normalized single-chain scattering function ($P(0) = 1$), and the magnitude of the scattering vector is $q = 4\pi\lambda^{-1} \sin (\theta/2)$ where θ is the scattering angle. The contrast factor K is given by

$$K = (B_D - B_H)^2 n_t \phi(1 - \phi) \tag{3}$$

where n_t is the total number of scattering centers (here chosen as C_4H_8 repeats) per unit volume, ϕ is the volume fraction of labeled chains, and $B_D - B_H$ is the difference in coherent scattering lengths of repeat units in the D-HPB and HPB polymers:

$$B_D - B_H = 8y(b_D - b_H) \tag{4}$$

In eq 4 the average fraction of deuterium on labeled chains is given by y, and $b_D - b_H = 1.041 \times 10^{-12}$ cm is the difference in coherent scattering lengths between deuterium and hydrogen.[11]

Table I
Radius of Gyration for Labeled HPB of M = 158000

sample	ϕ	R_g, Å	comment
D-HPB	0.11	215	this work
D-HPB/HPB	0.05	205	this work
DPB/HPB	0.50	209	ref 9
DPB/HPB	0.10	213	ref 9

The coherent SANS cross section for the undiluted D-HPB and the $\phi' = 0.5$ blend of D-HPB in HPB are shown in Figure 2. Most apparent is the considerable intensity from the exchanged sample, which, combined with the roughly 50% decrease in intensity on dilution with HPB, shows that $\phi << 1$ for undiluted D-HPB.

Before we proceed further, some attention should be given to the shapes of the scattering curves, from which we wish to evaluate the average size of the labeled scattering chains. Conventional Guinier or Zimm plots are not adequate, as the radius of gyration is too large for the q range accessible ($q > 0.007$ Å^{-1}). Therefore, the observed intensity profile was fitted to a Gaussian coil scattering function[12]

$$P(u) = 2u^{-2}[\exp(-u) - 1 + u] \tag{5}$$

where $u = q^2R_g^2$ and R_g^2 is the mean square radius of gyration of the chain. This method has been shown to be justified on HPB/DPB blends over a large range of molecular weights and at all concentrations, even though the polymer is ~40% crystalline.[2,9,10] The solid lines in Figure 2 represent the best fits to eq 5, and the dashed lines are obtained by varying R_g by ±30%. The largest intensities at low q are most reliable for this comparison, from which is is seen that R_g can be determined to within ±20%. The results are summarized in Table I, together with R_g obtained by the same method with HPB/DPB blends of polymers made by saturation of the identical parent polybutadiene used in the present experiments. It can be seen that R_g is the same in exchanged and directly deuterated systems. We conclude therefore that the exchange reaction effectively labels (some of the) chains over their entire length and furthermore does not cause any significant changes in chain dimension (i.e., scission or cross-linking). This latter point is confirmed by the essential constancy of $[\eta]$ mentioned above.

Since it appears that we are observing scattering from an unknown fraction of chains which are labeled uniformly, in a statistical sense, eq 2–4 can be employed to evaluate y and ϕ. The extrapolated intensity at $q = 0$, together with N from characterization of the parent polybutadiene, gives the product $y^2\phi(1 - \phi)$. The other required relation is provided by the overall extent of deuteration derived from density (eq 1), which may be written as

$$\langle y \rangle = y\phi = 0.065 \tag{6}$$

where ϕ is the volume fraction of labeled chains in the exchanged sample D-HPB. The results of this analysis are $y = 0.59$ and $\phi = 0.11$. The implied volume fraction is confirmed by the much lower intensity of the $\phi' = 0.5$ D-HPB/HPB blend; dilution by 50% is predicted to decrease the intensity to 0.53 of the value for the exchanged sample, in good agreement with the factor of 0.6 seen in Figure 2.

Conclusions

D–H exchange catalyzed by rhodium metal results in appreciable deuteration ($y = 0.6$) of about 10% of the saturated HPB chains under the conditions employed here. This reaction appears to proceed with no unwanted side reactions, i.e., chain scission or cross-linking. The chain dimensions inferred from SANS patterns are the same as those obtained from directly deuterated DPB, and the viscosity-average molecular weight is essentially unchanged by the exchange reaction. Given the fact that only a minority of the chains are exchanged, a fairly substantial change in N of the reacted macromolecules would lead to a modest change in $[\eta]$ in any case. Therefore, the constancy of R_g is considered more significant evidence that the skeletal chemistry of the HPB is unaffected by the D–H exchange reaction. This point will be checked more thoroughly with techniques such as gel permeation chromatography and melt rheology in future work.

The observation that only a small fraction of the chains are appreciably reacted is something of a surprise, though this probably results from the use of heterogeneous catalyst. We note, however, that a similar product distribution is obtained in analogous deuterium–exchange reactions involving *n*-hexane[13] and *n*-heptane[14] over metal catalysts. Addition reactions, on the other hand, appear to proceed more uniformly; saturation of polybutadiene with either H_2 or D_2 over a heterogeneous palladium catalyst results in quantitative addition to all chains.[9,15] It is clear that more experiments, including those using a deuterated solvent, are needed to improve the yield of labeled chains by exchange. Another point to be investigated is the possible dependence of exchange kinetics on molecular weight, as this would affect interpretation of SANS patterns of polydisperse samples prepared in this manner. Such work is currently under way.

This exchange technique should be applicable to other polyolefins and polymers containing olefinic sequences. The availability of a direct method for obtaining deuterated polymers will significantly expand the power of SANS experiments to study polymeric systems.

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References and Notes

(1) Boué, F.; Nierlich, M.; Liebler, L. *Polymer* **1982**, *23*, 29.
(2) Crist, B.; Graessley, W. W.; Wignall, G. D. *Polymer* **1982**, *23*, 1561.
(3) Willenberg, B. *Makromol. Chem.* **1976**, *177*, 3625.
(4) Gradjean, J. *Makromol. Chem.* **1977**, *178*, 1445.
(5) Willenberg, B. *Makromol. Chem.* **1977**, *178*, 2401.
(6) Linder, P. *Makromol. Chem.* **1981**, *182*, 3653.
(7) Kemball, C. In "Advances in Catalysis"; Academic Press: New York, 1959; Vol. 11, pp 223–62.
(8) Burwell, R. L., Jr. *Acc. Chem. Res.* **1969**, *2*, 289.
(9) Tanzer, J. D.; Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2702.
(10) Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2708.
(11) Kostorz, G.; Lovesey, G. In "Treatise on Materials Science and Technology: Neutron Scattering"; Academic Press: New York, 1979; Vol. 15, pp 5–8.
(12) Debye, P. *J. Phys. Colloid Chem.* **1947**, *51*, 18.
(13) Burwell, R. L., Jr.; Shin, B. K. C.; Rowlinson, H. C. *J. Am. Chem. Soc.* **1957**, *79*, 5142.
(14) Forrest, J. M.; Burwell, R. L., Jr.; Shin, B. K. C. *J. Phys. Chem.* **1959**, *63*, 1017.
(15) Rachapudy, H.; Smith, G. G.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1211.

Deformation Behavior of Styrene–Butadiene–Styrene Triblock Copolymer with Cylindrical Morphology

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ABSTRACT: Morphological changes related to deformation of styrene–butadiene–styrene block copolymers with a cylindrical microdomain structure have been studied by small-angle X-ray scattering. The behavior of originally isotropic, solution-cast samples has been compared with the deformation and related structural changes of samples with original macroscopically oriented morphology. The structure related to various stages of deformation has been determined from SAXS patterns by considering separately changes in the single-particle scattering and changes in the lattice factor, both of which influence the scattering patterns. The early and intermediate stages of deformation of the triblock copolymer are controlled by its morphology, while at large extensions the deformation and resulting structure are determined by molecular orientation in the polybutadiene phase.

I. Introduction

Peculiar mechanical properties of triblock styrene–butadiene–styrene (SBS) polymers have been observed by many authors.[1-8] When stretched, in some cases, these polymers initially show a stress–strain dependence similar to those of glassy polymers drawn below the glass transition temperature. Beyond the yield point, however, the SBS polymer becomes rubbery with high elasticity and large recoverable deformation.[4-8] Moreover, after stretching and especially upon annealing after removal of the external stress, the specimens can show a healing effect in that properties of the original undeformed state are recovered.[4-8] Attempts have been made to explain these effects on the basis of structural changes at various stages of deformation. The strain-induced plastic-to-rubber transition in SBS block copolymers has been attributed to fragmentation of the originally rigid structure by large plastic deformation of the glassy component. The healing process has been attributed to the reformation of the original structure.[5-7] The understanding of the deformation mechanism in this type of polymer is, however, still not satisfactory.

Detailed consideration of these effects must take into account the morphology of these polymers, which is highly heterogeneous and ordered on various dimensional levels. Figure 1 shows schematically the cylindrical microdomain

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