Macromolecules 1992, 25, 5026–5029

Stress and Birefringence Relaxations of Noncrystalline Linear Polymer

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Received February 18, 1992; Revised Manuscript Received May 20, 1992

ABSTRACT: Internal stresses in noncrystalline, linear polymer materials arise from two different sources: deviation of polymer conformation from its equilibrium state and change of intersegment distances. The separation of the two components in stress relaxation by simultaneous measurements of tensile stress and birefringence was carried out over the temperature range from the glassy state to the terminal zone, using three samples of polystyrene with different molecular weights. The master curves and relaxation spectra of the two stress components were constructed from the data. Discussion was given to the relaxation spectra for conformational deformation.

1. Introduction

The viscoelastic properties of noncrystalline, linear polymers in the undiluted state such as stress relaxation, creep, etc., are now well clarified based on the molecular dynamics of the macromolecules if the temperature is above, roughly speaking, the glass transition temperature, T_g. The motions of the macromolecules and their constituting segments or the relaxation times describing the viscoelastic behavior are, at least qualitatively, explained by the modified theory of Rouse and Zimm.[1] That is, the stresses observed in tensile stress-relaxation experiments arise from deformation of the macromolecules from their equilibrium states if the temperature is above T_g. The deformation of polymer chain conformations also causes birefringence if there is an anisotropy in the polarizabilities of constituting elements. It is well-known that the results of the birefringence method obtained for rubbers are consistent with the results of stress measurements.

In the glassy state, however, the situation is entirely different. As the temperature is decreased below T_g, the relaxation times τ governing the viscoelastic properties of the sample in the usual experimental ranges become shorter. From the viewpoint of molecular dynamics this is understood such that only the local motions of polymer chains become predominant in viscoelastic behavior. In the modified theory of Rouse and Zimm, the spectrum of relaxation times $H(\tau)$ increases with decreasing τ according to the following relationship.

$$H(\tau) \propto \tau^{-1/2} \tag{1}$$

In experiments, however, the proportionality in eq 1 is observed only over a very limited range. It is clear that the modified theory of Rouse and Zimm is not sufficient for understanding viscoelastic properties of linear polymers below T_g.

In stress-relaxation experiments, the stress-relaxation modulus E approaches the modulus of a glass asymptotically as the temperature T decreases. At the limit of low temperature and/or at the limit of short observation time, the stress-optical coefficient C is entirely different from that in the molten or rubbery region. In the case of polystyrene employed as the sample in the present experiment, even its sign is different in the two regions. At the limit of low temperature and/or short observation time, the molecular motion of macromolecules is believed to be fully frozen, and, hence, the most plausible cause for the optical anisotropy induced by externally applied forces may be in the changes of the intersegment distances, just as in the stress-optical phenomena in low-molecular-weight materials. If an anisotropy in density appears in polymer materials due to external forces, it must cause a birefringence. In general, therefore, it may be assumed that two different kinds of deformation can occur in the glassy state of linear polymers. One is the deformation of the molecular conformation of the polymer, i.e., the deviation of the molecular conformation from its equilibrium state, which is now well-known to be close to the unperturbed random coil. The other is the density anisotropy arising from changes of intersegment distances in the material.[2] Moreover, it was also pointed out in the previous paper[2] that the changes of intersegment distances can occur immediately with extension of the film, but the deformation of the molecular conformation is gradually induced. Although the understanding of the mechanism is different, it was already pointed out in previous works[3,4] that a different type of deformation having a different stress-optical coefficient from that in the rubbery and molten regions is to be brought in for understanding the rubber–glass transition behavior.

As in the previous paper,[2] the stress and stress-optical coefficients originating in the deformation of the molecular conformation and in the changes of intersegment distances are expressed by subscripts r and g, respectively. Following previous works,[2,4] let us assume that the two kinds of stresses, σ_r and σ_g, are additive

$$\sigma(t) = \sigma_r(t) + \sigma_g(t) \tag{2}$$

Then, the birefringence Δn is also additive

$$\Delta n(t) = C_r\sigma_r(t) + C_g\sigma_g(t) \tag{3}$$

since the extinction angle would agree with the direction of elongation in tensile stress-relaxation experiments. If we can employ the above assumptions, the two stress components could be separated by carrying out simultaneous measurements of birefringence and tensile stress or some corresponding quantities.[3,4]

The purpose of this work is to investigate the details in the contributions of σ_r and σ_g to the total stress σ, by determining their master curves and relaxation spectra. For this purpose simultaneous measurements of tensile strength and birefringence relaxations of polystyrene films not only in the glassy state but also in the rubbery and terminal zones are carried out with three samples with different molecular weights.

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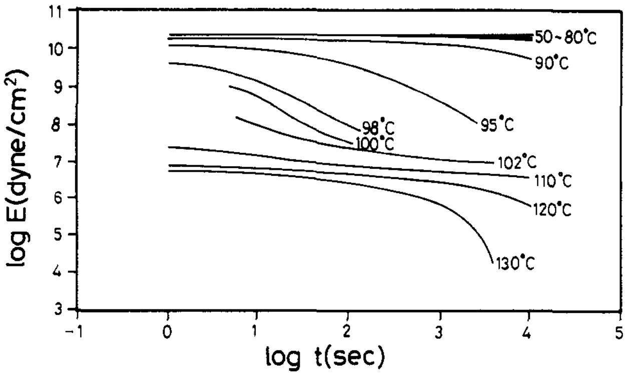

Figure 1. Double-logarithmic plots of the tensile relaxation modulus E vs time t at various temperatures for sample A.

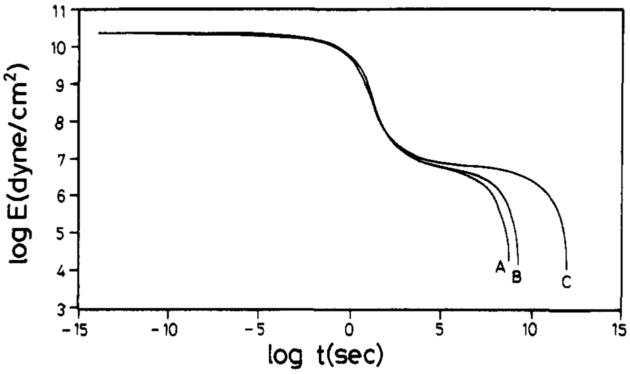

Figure 2. Master curves of the tensile relaxation moduli E. The sample numbers are shown in the figure. T_0 = 100.0 °C.

2. Experimental Section

2.1. Samples. The polystyrene samples with three different molecular weights used in the present work were prepared by an anionic polymerization method. The weight-average molecular weight, M_w, and the polydispersity index, M_w/M_n, of each sample were determined by a Tosoh liquid chromatograph HLC 802, using four columns of TSK GEL G-4000HXL or G-6000HXL and TSK standard polystyrenes. The values of M_w and M_w/M_n obtained are 2.4 × 10^5 and 1.05 for sample A, 4.4 × 10^5 and 1.10 for sample B, and 10.8 × 10^5 and 1.15 for sample C, respectively. The stress-optical coefficients of polystyrene are C_g = +8.3 × 10^{-13} [2,5] and C_r = −5.0 × 10^{-10} cm²/dyn.[6,7]

Films of the samples, which were cast by the same method as before,[2] were dried in vacuo, raising the temperature from room temperature to T_g +20 °C. The remaining amounts of solvent (benzene) in the films were estimated to be less than 0.14, 0.23, and 0.42% for samples A, B, and C, respectively, by comparing the film weights with the weights after drying in vacuo at 180 °C for 24 h. Since the sample films used in the previous work[2] contained about 3.1% of toluene, the previous data cannot quantitatively be compared with the present data.

2.2. Measurements. The ellipsometer and the apparatus for simultaneous measurements of stress and birefringence relaxations used in this work were the same as those reported in the previous work,[2] except that the ellipsometer was set horizontally so that a sample film may be located perpendicularly. The temperature was maintained within ±0.2 °C by PID controllers in the range from 50 °C to the terminal zone.

3. Experimental Results

Tensile relaxation modulus E for sample A, calculated from observed tensile stress σ and the degree of elongation given to the sample ϵ, is double-logarithmically plotted against time t at various temperatures in Figure 1. Figure 2 shows a master curve obtained by superimposing those curves upon the curve at a reference temperature, 100.0 °C, according to the time–temperature superposition principle.[1] The master curves for the other samples B and C are also shown in Figure 2.

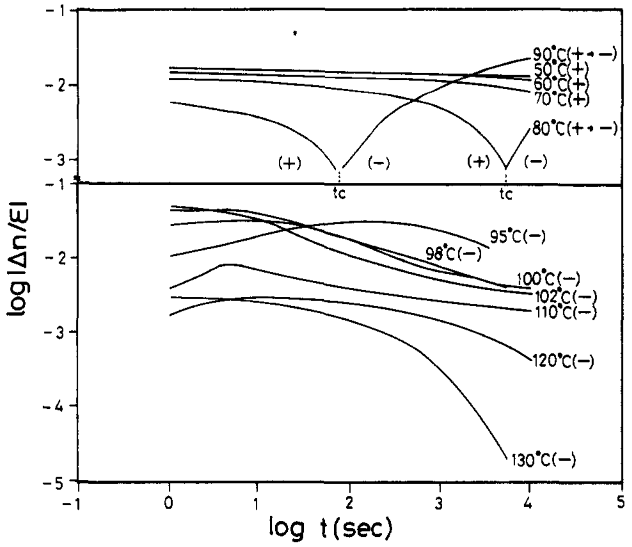

Figure 3. Double-logarithmic plots of $|\Delta n|/\epsilon$ vs time t at various temperatures for sample A. + and − in the figure show the sign of $\Delta n/\epsilon$.

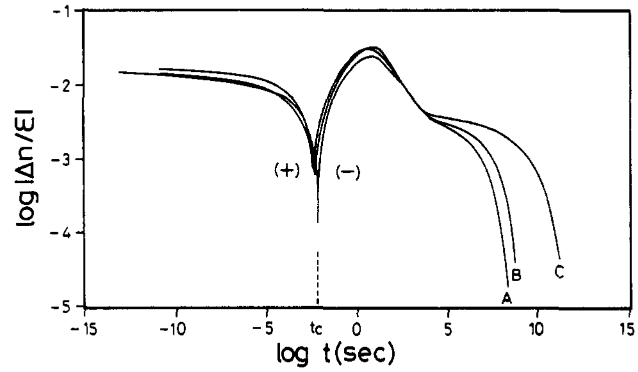

Figure 4. Master curves of log ($|\Delta n|/\epsilon$) vs log t plot. The sample numbers are shown in the figure. T_0 = 100.0 °C.

The ratio of birefringence to strain $\Delta n/\epsilon$ for sample A, observed simultaneously with tensile stress, is plotted against time t in a double-logarithmic way in Figure 3. As was pointed out in the previous paper,[2] $\Delta n/\epsilon$ is positive at lower temperatures, while it is negative at higher temperatures. In the vicinity of 90 °C, the birefringence changes its sign from positive to negative with time, implying that the intersegment distances are changed immediately after a strain is given to the film, whereas the conformational deformation is gradually induced. To make their features clearer, a master curve of log ($|\Delta n|/\epsilon$) vs log t is constructed from the data in Figure 3, choosing 100.0 °C as a reference temperature T_0. The master curve of $|\Delta n|/\epsilon$ of sample A thus constructed is shown in Figure 4, together with those for the other samples B and C. In the longer time region, $|\Delta n|/\epsilon$ shows the molecular weight dependence similar to that of relaxation modulus E in Figure 2. In the shorter time region it is observed that $\Delta n/\epsilon$ changes its sign from positive to negative at a time t_c.

The apparent stress-optical coefficients C, which is defined as the ratio between birefringence and stress observed at the same time, also form smooth master curves as shown in Figure 5. It may be concluded that the apparent stress-optical coefficient C is independent of molecular weight. The limiting value of C at $t \rightarrow 0$ is positive and agree with the value of C_g in the literature,[5] whereas the value at longer times is negative and agrees with the value of C_r in the literature.[6,7] It is observed that C changes its sign from positive to negative at a time t_c. Figure 5

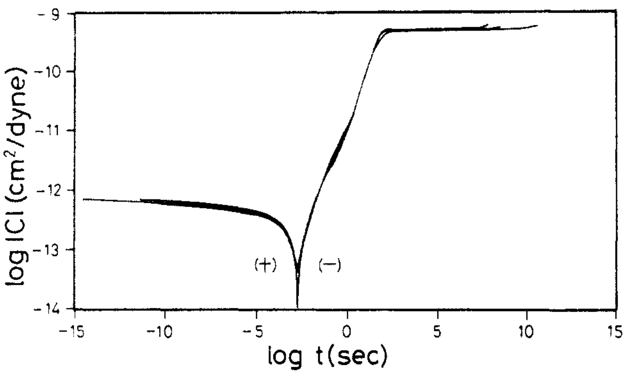

Figure 5. Master curves of the apparent stress-optical coefficient C of three samples with different molecular weights. + and − show the sign of C.

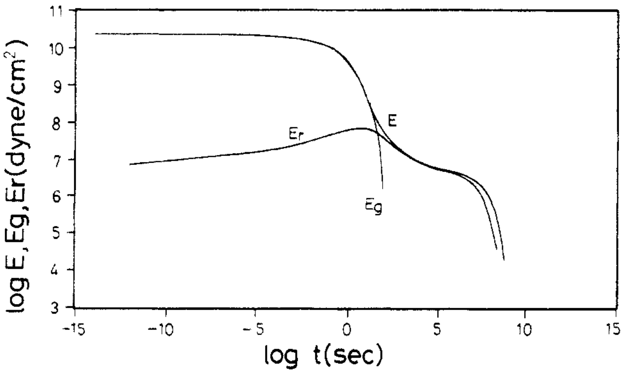

Figure 6. Comparison among master curves of E_g, E_r, and E for sample A. T_0 = 100.0 °C.

shows that the apparent stress-optical coefficient for linear polymers is not only a function of temperature but also a function of time.

By inserting the data of σ and $\Delta n/\epsilon$ into eqs 2 and 3, assuming the literature values for C_r and C_g, we can obtain two components of stress, σ_r and σ_g. Two components of relaxation moduli E_r and E_g can be calculated if we assume that the strains for σ_r and σ_g are both equal to the strain given to the film ϵ. The master curves of the two stress components can be constructed by the same method as for E. The contributions of E_r and E_g thus determined to E are compared in Figure 6. It can be pointed out from the figure that the relaxation modulus E is mainly determined by E_g in the shorter time region, whereas it is determined by E_r in the rubbery and terminal zones. E_g is constant in the shorter time region or at lower temperatures and drops sharply in the vicinity of T_g. On the other hand, the conformational component E_r shows a gradual increase with increasing t. After showing a maximum at about T_g, E_r decreases in a way similar to the total relaxation modulus E. The master curves E_g and E_r for three samples with different molecular weights are summarized in parts a and b of Figure 7, respectively. No molecular weight dependence is found for E_g. The molecular weight dependence of E_r in the range from the rubbery to the terminal zone is similar to that of E.

The shift factors assumed in constructing respective master curves are summarized in Figure 8. In this work, those shift factors were chosen to make each master curve most smooth, without referring to the other master curves. The choice of shift factors for E and E_g in the glassy region may be arbitrary since the curves are so flat. Above T_g the shift factors thus chosen agreed with each other not only among the samples but also among different kinds of measurements. Below T_g, however, the shift factors thus chosen scattered considerably. Since the log E_g vs log t curve is flat in the glassy region, moreover, it cannot be determined whether or not there is any difference between the shift factors for E_r and E_g. A WLF equation shown in Figure 8 was determined to give the best fit with the E_r data in the range between 102 and 170 °C. It is reasonable that all the shift factors for different physical quantities, E, E_r, and $\Delta n/\epsilon$, can be expressed by the same WLF equation if the temperature is higher than T_g, since the strain in the film is only due to the deformation in the molecular conformation if $T > T_g$.

Using Schwarzl and Staverman's second approximation method,[8] the logarithmic relaxation spectra log $H_g(\tau)$, log $H_r(\tau)$, and log $H(\tau)$ were calculated from the data of the corresponding master curves of log $E_g(t)$, log $E_r(t)$, and log

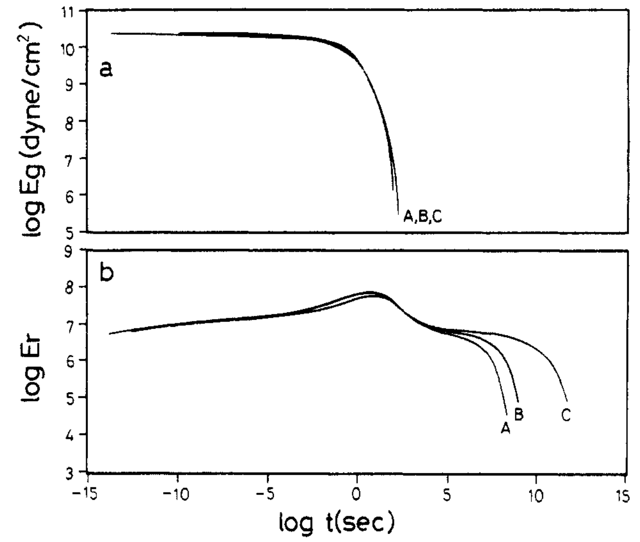

Figure 7. Molecular weight dependence of the master curves of $E_g(t)$ (a) and $E_r(t)$ (b). The sample numbers are shown in the parts of the figure. T_0 = 100.0 °C.

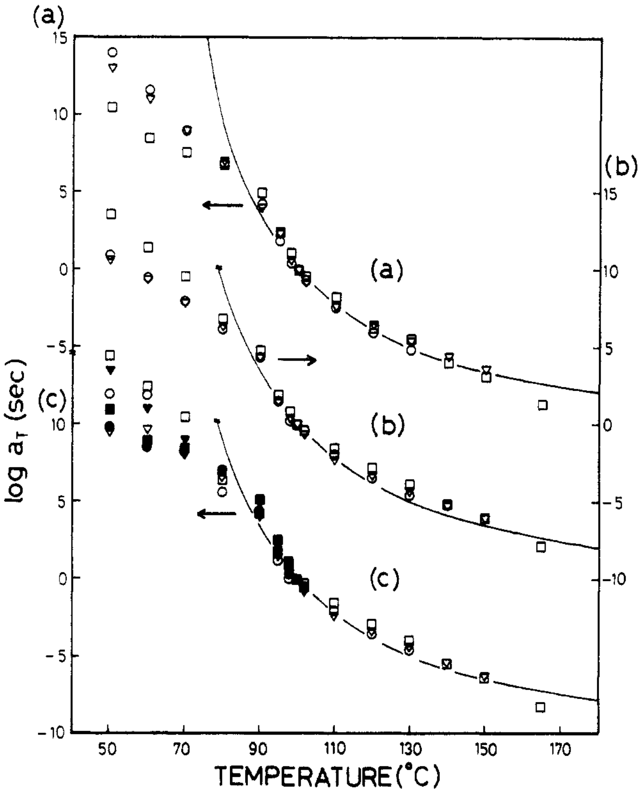

Figure 8. Shift factors a_T for E (a), for $|\Delta n|/\epsilon$ (b), and for E_g (filled) and E_r (open) (c) for samples A (○) B (▽), and C (□). The solid lines show a WLF equation determined from the data of E_r; log $a_T = -12.5(T - T_0)/[47.26 + (T - T_0)]$ and T_0 = 100.0 °C.

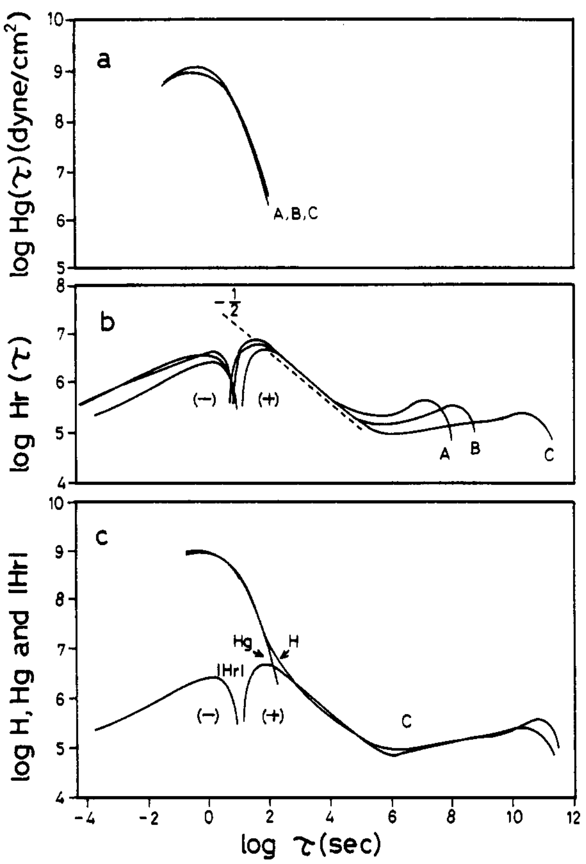

Figure 9. Relaxation spectra $H_g(\tau)$ (a) and $H_r(\tau)$ (b) and comparison of $H_g(\tau)$ and $H_r(\tau)$ with $H(\tau)$ (c). The slope $-1/2$ shows a prediction of the theory of Rouse and Zimm.[1] + and − show the sign of H_r. The sample numbers are shown in the figure.

$E(t)$ vs log t plots, respectively. The former two spectra are shown in parts a and b of Figure 9, respectively, and three spectra for sample C are compared with each other in Figure 9c. The shape of log $H_g(\tau)$ is reasonable since there should not be so many modes in the changes of intersegmental distances. The log $H_r(\tau)$ vs log τ plots in Figure 9b show typical features for polymers with narrow molecular weight distributions in the rubbery and terminal zones.[9-13] Moreover, they give a slope of $-1/2$ in the transition region in agreement with the prediction of molecular theories,[1] as was pointed out by Read,[4] Priss,[3] and Osaki et al.[14] In the shorter time region, i.e., in the glassy region, however, the spectrum of log $H_r(\tau)$ is quite unreasonable. That is, $H_r(\tau)$ becomes negative. The problem will be discussed in the following section. In Figure 9b, the absolute values of $H_r(\tau)$ are shown for convenience of discussion.

4. Discussion

The conclusions in the glassy region obtained above are in agreement with the conclusions reported before.[2] In the glassy region, it is certain that changes in intersegment distances can occur immediately with extension of films, but the deformation of the molecular conformation does not instantly occur but is gradually induced. The molecular conformation is extended gradually as the extended intersegment distances shrink. The behavior appears as if the two mechanisms were combined in series. Although the interaction between the two mechanisms should be carefully studied in the future, it is at least certain that eq 2 is one of the rather questionable assumptions in the glassy region.

However, the failure of the assumption in eq 2 is not a main reason for the abnormal values of $H_r(\tau)$ in the glassy region in the present experiments. In the present case where $|C_r| \gg |C_g|$, eqs 2 and 3 give

$$\sigma_r(t) = \frac{(C - C_g)}{C_r}\sigma(t) \qquad (4)$$

The relationship of eq 4 can be obtained directly from eq 3 without assuming eq 2 if $\sigma_g(t) \approx \sigma(t)$ in the glassy region. Therefore, $\sigma_r(t)$ obtained in the present work are reliable. The problem may occur in converting $\sigma_r(t)$ into $E_r(t)$. It is assumed in calculating $E_r(t)$ that the polymer coils were extended by the same amount as the strain of the film ϵ. The assumption of affine deformation is surely unapplicable if there is a delay in the transformation of the molecular conformations in the glassy state. The unreasonable $H_r(\tau)$ in Figure 9b in the glassy region clearly arises from the assumption of affine deformation of the molecular conformation. However, it is difficult to determine where the assumption starts to fail as time t is decreased.

In the above analysis of data, it is assumed that only two kinds of deformations, deformation of the molecular conformation and changes in the intersegment distances, are induced in the extension of amorphous polymer films. As were sometimes assumed in previous works, there may be possibilities that other types of deformation such as movements of side chains are involved. That is, the intrinsic anisotropy of the monomers may be affected by external forces in the transition region. At least in the range of the present experiments, however, the assumption of the dual-deformation mechanism does not cause any contradiction in the analysis of experimental data. The limiting value of stress-optical coefficient at $T \rightarrow 0$ and $t \rightarrow 0$, that is, the limiting value at log $t \rightarrow -\infty$ in Figure 5, is so far different from C_r that it can hardly be believed to be due to a change in the intrinsic anisotropy of the monomer.

Acknowledgment. We thank Professor Matsuura of Kanazawa University for his helpful advices in measurements.

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Registry No. Polystyrene (homopolymer), 9003-53-6.