

Small-Angle Neutron Scattering from Deuterated Polystyrene in Dioctyl Phthalate Solution under Shear

B. Hammouda,*† A. I. Nakatani,† D. A. Waldow,† and C. C. Han†

Materials Science and Engineering Laboratory, Reactor Radiation and Polymers Divisions, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received October 4, 1991; Revised Manuscript Received January 6, 1992

ABSTRACT: Small-angle neutron scattering measurements were taken from high molecular weight (1.95×10^6) deuterated polystyrene in dioctyl phthalate solution at low concentration (3% weight fraction) under steady shear with rates ranging from the quiescent condition (0 s^{-1}) to 1100 s^{-1} at room temperature ($22 \text{ }^\circ\text{C}$). The scattered intensity increased drastically beyond a characteristic shear rate ($\dot{\gamma}_c = 57 \text{ s}^{-1}$) similar to the increase following a temperature drop from the one-phase region (ambient temperature) to the two-phase region in this upper critical solution temperature system. The cloud point is estimated to be a few degrees lower than $14 \text{ }^\circ\text{C}$ which is the cloud point for protonated polystyrene in dioctyl phthalate at this molecular weight and concentration. On the basis of this analogy, the random-phase approximation (RPA) approach (the Zimm inverse scattering formula) was used along with a swollen radius of gyration in the Debye function to analyze the data and extract a statistical segment length b and a polymer-solvent interaction parameter χ_{ps} . The segment length was seen to increase slightly, indicating a slight increase in chain volume beyond $\dot{\gamma}_c$, while the interaction parameter showed a dramatic increase up to the "spinodal" value $\dot{\gamma}_s = 280 \text{ s}^{-1}$ where the RPA breaks down, therefore giving nonreliable values. This data treatment method has no justification on physical grounds: it is merely a way to quantify our observations since specific models that could explain our data are not available at this time.

Introduction

Previous investigations^{1,2} have demonstrated that solutions of high molecular weight polystyrene in certain solvents become turbid with the application of a sufficiently large steady shear. This effect has been observed in a wide variety of polymer/solvent systems. Such shear-induced temperature "shifts" were discussed as early as 1952.³ An accepted explanation of this phenomenon has not been found despite numerous experimental and theoretical efforts (see Results and Discussion). The purpose of the experiments reported here is to apply the small-angle neutron scattering (SANS) technique in order to investigate the steady-state "apparent" thermodynamics (the Flory-Huggins interaction parameter) of a 3% solution of high molecular weight deuterated polystyrene (PSD) in dioctyl phthalate (DOP) under steady shear. It is assumed here that steady state can be approximated as an equilibrium state so that the Flory-Huggins interaction (χ) parameter is obtained as a function of shear rate. Light scattering experiments have been conducted in this laboratory on a protonated polystyrene with the same molecular weight and concentration in DOP. A marked increase in sample turbidity was observed above 165 s^{-1} , which is consistent with other investigations.^{1-2,4} The SANS technique, though, had not yet been applied to this problem.

Previous SANS studies of polymer systems under shear showed an apparent shear-induced mixing in blends of low molecular weight PSD/polybutadiene (upper critical solution temperature system) and PSD/poly(vinyl methyl ether) blends⁵ (lower critical solution temperature system). An apparent shift in the phase boundary occurred only in the direction parallel to flow. Shearing is, therefore, not equivalent to a simple effective temperature shift but involves a more complicated interplay between hydrodynamic and thermodynamic effects.

De Gennes' random-phase approximation (RPA) theory^{6,7} describes scattering from concentrated polymer

solutions. This mean-field theory (RPA assumes linear response and mean fields) describes the polymer-solvent interactions through a phenomenological χ parameter. Here, χ is adjusted to fit our shear data in the spirit of many other experimental studies,⁸⁻¹² where it was found to depend on temperature, molecular weight, composition, intermonomer distance (and therefore on Q), isotopic constitution, tacticity, microstructure, etc. The limitations of the RPA theory are well-known (even for quiescent systems), and our procedure for adjusting χ is merely a concise means of summarizing our observations.

A number of investigators have demonstrated the utility of the RPA for polymer melts and blends. Zimm's inverse scattering formula¹³ is also a statement of the RPA (even though this was not recognized at the time of its discovery) for dilute polymer solutions. The extension of the Zimm formula by Benoit and Benmouna¹⁴ models concentrated polymer solutions and polymer melts through "chains" of single contacts whereby two polymer chains can interact through a series of binary single contacts. The Zimm formula which is a mean-field result is a major tool (Zimm plots) for extracting single-chain properties from polymer solutions.

In this work, the RPA will be used to describe the scattering from a dilute solution of high molecular weight PSD in DOP under shear. This approach is equivalent to assuming that shear affects the monomer-solvent interaction (χ) parameter only. This simplified picture cannot be true, and hydrodynamic effects on chain conformations must also be important. Theoretical models exist in the literature in order to understand scattering data from high molecular weight polymers under shear. Helfand and Fredrickson¹⁵ have used a set of coupled hydrodynamic equations with inhomogeneous transport coefficients (shear viscosity and normal stress coefficients) to describe the dynamics of concentration fluctuations of polymer solutions (using Rouse dynamics) in the presence of simple shear flow. Onuki¹⁶ included polymer elastic terms that yielded a shear-induced temperature shift to higher temperatures. Milner¹⁷ has extended the Helfand-Fredrickson work¹⁵ to the case of entangled polymers. All these

* Reactor Radiation Division, Building 235, E 151.

† Polymers Division, Building 224, B 210.

Table I
Results of the Fit to the SANS Data

shear rate $\dot{\gamma}$, s ⁻¹	segment length b , Å	interaction parameter χ_{ps}/ν_0	correlation length ξ , nm
0.00	7.2	9.7×10^{-3}	16.5
0.323	7.2	9.7×10^{-3}	16.3
0.576	7.2	9.7×10^{-3}	17.1
1.026	7.1	9.7×10^{-3}	16.7
1.821	7.1	9.7×10^{-3}	17.5
3.23	7.1	9.8×10^{-3}	15.7
5.76	7.1	9.7×10^{-3}	14.0
10.26	7.2	9.5×10^{-3}	13.3
18.21	7.2	9.6×10^{-3}	13.8
32.33	7.3	9.7×10^{-3}	14.5
57.60	7.5	9.7×10^{-3}	16.5
102.51	8.0	10.5×10^{-3}	17.8
181.96	8.9	12.1×10^{-3}	17.4
323.32	8.8	13.4×10^{-3}	34.5
576.01	7.8	13.5×10^{-3}	44.2
247.04	9.0	12.5×10^{-3}	19.9
323.32	8.7	13.4×10^{-3}	36.9
414.73	8.3	13.5×10^{-3}	64.2
650.0	7.5	13.4×10^{-3}	no fit
718.2	no fit	no fit	no fit
1100.0	no fit	no fit	no fit

models assume low scattering momentum transfer and can be used to interpret light scattering data under shear (which is anisotropic). These, however, cannot be used to interpret SANS data under shear which turns out to be isotropic probably because of the contribution from internal Brownian modes (one single diffusive mode can be assumed only at low Q).

Experimental Section

Deuterated polystyrene (PSD) (manufacturer supplied, $M_w = 1.95 \times 10^6$, $M_w/M_n = 1.14$) was obtained commercially (Polymer Laboratories Ltd.).¹⁸ Gel permeation chromatography (GPC) of the polymer showed a protonated polystyrene equivalent molecular weight of 1.81×10^6 and $M_w/M_n = 1.64$. The PSD was dissolved in DOP to a 3% polymer weight fraction (2.83% polymer volume fraction). This corresponds to a concentration below the overlap concentration C^* which is equal to 5.7% according to the definition $C^* = M_w/R_g^3 N_{av}$. Note that, if the alternative definition $C^* = 3M_w/4\pi R_g^3 N_{av}$ is used, then our solution is in the semidilute region. The published cloud-point curve¹ for a 3% solution of protonated polystyrene in DOP indicates a cloud point of 14 °C (the cloud point for PSD is expected to be a few degrees lower). Since all SANS measurements were performed at ambient temperature (22 °C), the quiescent solution was well in the one-phase region.

The shear apparatus¹⁹ used here is composed of a set of coaxial cylinders with a nominal gap of 0.5 mm and is equipped with two separate motors which allow a range of shear rates between $\dot{\gamma} = 0.02$ and 7000 s⁻¹ and a maximum torque capacity of 67 N·m. Measurements were made at shear rates ranging from 0 to 1100 s⁻¹ corresponding to motor speeds of 0–110 rpm. Logarithmic steps between the shear rates were used to cover this wide range. The counting time for each motor speed was 3 h. Upon completion of a particular motor speed, the next speed was applied without any delay time. The shear rate was systematically increased up to 323.3 s⁻¹. For shear rates higher than 323.3 s⁻¹, the shear rates were varied nonsystematically to check whether nonreversible effects (due to chain scission, for example) exist. The chronological order of runs is shown in Table I. Comparison of two separate runs at 323.3 s⁻¹ shows no difference in the scattering behavior. At the conclusion of all SANS experiments, GPC was performed on the used sample. The protonated polystyrene equivalent molecular weight was 1.45×10^6 and $M_w/M_n = 1.70$, indicating that some mechanical degradation of the sample occurred in the course of the experiment (probably at the higher motor speeds).

SANS experiments were performed on the new 30-m NG7 SANS instrument at the National Institute of Standards and Technology Cold Neutron Research Facility (NIST-CNRF). The

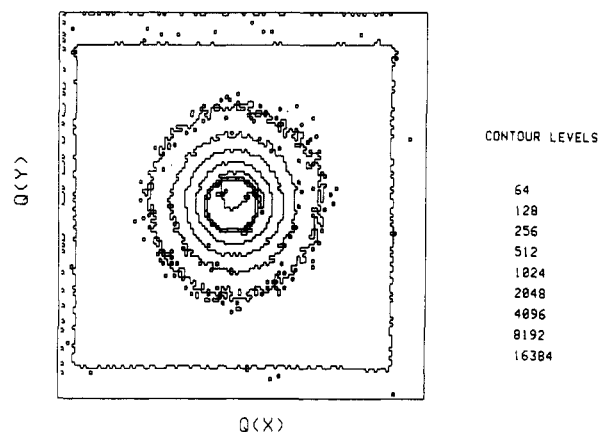


Figure 1. Isointensity contour maps of the SANS intensity for a shear rate of 323.32 s⁻¹.

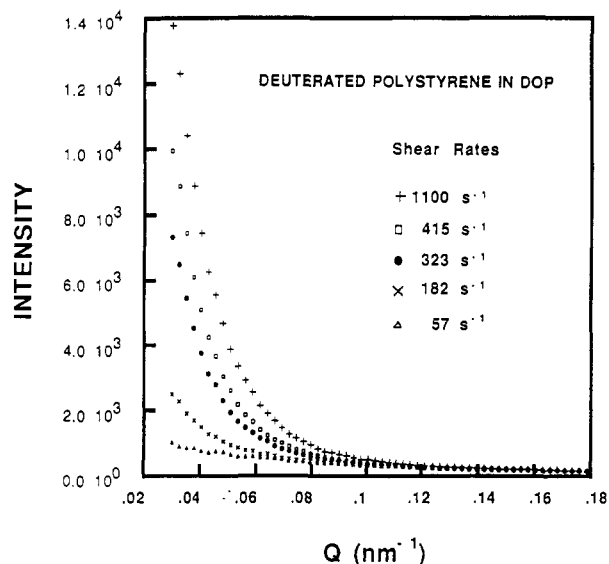


Figure 2. Corrected and reduced SANS data from PSD in DOP solution for some of the measured shear rates. The intensity is in an arbitrary scale.

instrument was used in the following configuration: 15-m sample-to-detector distance, 0.8-nm wavelength, 11% wavelength resolution, 38- and 12-mm source and sample apertures, respectively. This choice was dictated by the large size of the PSD chains and the low polymer concentration. The shear cell was mounted on the secondary sample stage which consists of a Huber table with lateral positioning. This second sample position allows the use of bulky sample environments with minimal modifications to the instrument. SANS transmissions were measured for more than one shear rate and did not change appreciably with shear rate.

Treatment of the SANS Data

The SANS data were corrected for empty cell and beam blocked background scattering. Scattering from pure DOP solvent was also rescaled and subtracted. The scattering was isotropic for all shear runs including those corresponding to the highest shear rates as evidenced from isointensity contour maps (Figure 1) and from sector averaging of the data in horizontal and vertical directions. This fact justified a circular averaging of the data. Figure 2 shows the corrected data for a few runs. Since no absolute intensity calibration standard for this low- Q region was available to us at the time, our data were left on an arbitrary scale. The reduced and averaged SANS intensity, $I(Q)$,

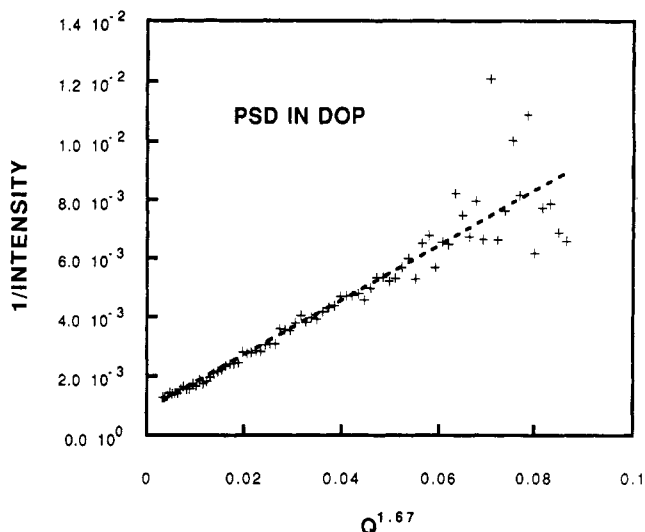


Figure 3. Plot of $1/I(Q)$ vs $Q^{5/3}$ (equivalent to the Zimm plot for a good solvent).

was fitted to the RPA form

$$(b_p/v_p - b_s/v_s)^2/I(Q) = 1/N_p\phi_p v_p D(Q) + 1/\phi_s v_s - 2\chi_{ps}/v_0 \quad (1)$$

where the usual notation has been used for the polymer (solvent) scattering length b_p (b_s), monomer volume v_p (v_s), volume fraction ϕ_p (ϕ_s), degree of polymerization N_p , interaction parameter χ_{ps} , and the Debye function for swollen chains $D(Q)$:

$$D(Q) = 2[\exp(-U) - 1 + U]/U^2 \quad (2a)$$

$$U = Q^2 b^2 N^{2\nu} / (2\nu + 1)(2\nu + 2) \quad (2b)$$

ν is the excluded-volume parameter. For $\nu = 0.5$, one recovers the usual Debye function, and for $\nu = 0.6$ one obtains the result for fully swollen chains. The full structure factor for swollen chains involving incomplete γ functions²⁰ was not used because of the large computational times required for its generation and because the Debye function approach with a swollen radius of gyration is often used to describe polymer coils in solution.

Nonlinear least-squares fits to the data were made using eqs 1 and 2 with $\nu = 0.6$. The fitting parameters were allowed to vary sequentially within estimated reasonable ranges. A small constant background and an intercept were obtained from fits to the quiescent state (zero-shear) data and were fixed to the same values for all subsequent runs leaving only two floating parameters: the statistical segment length b and the interaction parameter χ_{ps} . Results of the fits are listed in Table I.

A correlation length, ξ , has been extracted from Zimm plot fits to the data and has also been included in Table I. ξ has been obtained from linear fits to plots of $1/I(Q)$ vs $Q^{1/\nu}$ (with $\nu = 0.6$) which show a linear behavior (unlike plots of $1/I(Q)$ vs Q^2). Figure 3 shows such a plot for the quiescent case. This behavior shows the curvature for high shear rates, and the extracted correlation length ξ should not be taken too seriously.

Results and Discussion

The scattering behavior between 0.323 and 57.6 s^{-1} showed no discernible differences compared to the zero-shear rate scattering behavior. The fact that the SANS data were isotropic is in agreement with preliminary measurements reported by Lindner and Oberthur,²¹ who observed no anisotropy in the SANS contour maps for

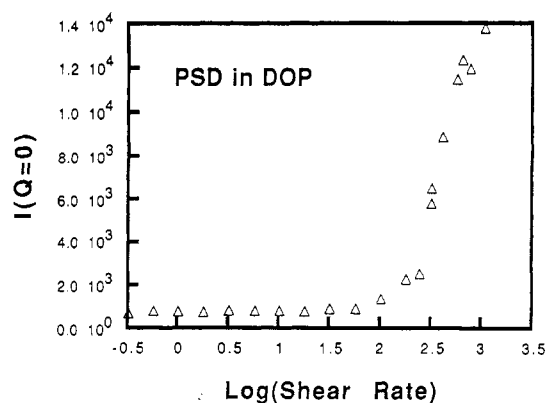


Figure 4. Variation of the low- Q ($Q = 0.032 \text{ nm}^{-1}$) intensity with shear rate.

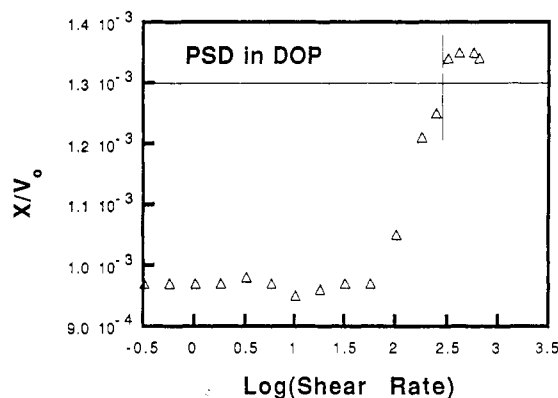


Figure 5. Variation of the extracted polymer-solvent interaction parameter χ_{ps} with shear rate. The horizontal line corresponds to the RPA predicted "spinodal" line.

high molecular weight (1.8×10^6) PSD in dilute solutions of oligostyrene/toluene mixtures. Their main experiments focused on chain conformations of lower molecular weight polystyrene in solution where they observed anisotropy. As shown in Figure 2, for shear rates greater than 57 s^{-1} , the low- Q scattering intensity increases with increasing shear rate up to the highest measured shear rate of 1100 s^{-1} .

The results of the fitting procedures are summarized in Table I. The fits were good (converged rapidly) for shear rates where no change in the scattering behavior is observed. As the apparent "spinodal" point is approached, the scattering intensity at low Q diverges (Figure 4), giving an estimate for the effective interaction parameter at the apparent spinodal line, $\chi_{ps}^s/v_0 = 1/2N_p\phi_p v_p + 1/2\phi_s v_s \sim 1.3 \times 10^{-3}$, and therefore of the apparent spinodal point at $\dot{\gamma}_s = 280 \text{ s}^{-1}$. As shown in Figure 5, the extracted interaction parameter increases with increasing shear rate. Beyond the value χ_{ps}^s , the extracted χ_{ps} parameters are not reliable. Moreover, it is interesting to note that $I(0)$ and χ_{ps} show a steep variation beyond a characteristic shear rate (around $\dot{\gamma}_c = 57 \text{ s}^{-1}$) which is still below $\dot{\gamma}_s$. The segment length b was seen to increase slightly with increasing shear rate, indicating a slight augmentation in chain volume between $\dot{\gamma}_c$ and $\dot{\gamma}_s$ (believed to be real). Beyond $\dot{\gamma}_s$ the breakdown of the RPA model is manifested as a lowering of the values of b (which is believed not to be a real effect) along with a worsening of the fits.

Our interpretation of the data depended heavily on the inverse scattering Zimm formula which is a mean-field result. Arguments have been presented in the literature^{15-17,22} that (dilute or semidilute) polymer solution thermodynamics do not follow the mean-field theory due to the increased influence of fluctuation effects. For

example, the mean-field approach predicts that no true shift in the phase boundary should occur as a result of the application of a steady shear. Our use of the mean-field approach for polymer solutions under shear (as well as the common use of Zimm plots) is not rigorously justified and was resorted to because of the lack of appropriate models to describe our SANS data. A number of authors, Helfand and Fredrickson,¹⁵ Onuki,¹⁶ Milner,¹⁷ and Pistor and Binder²² have developed models (most of them based on mode-mode coupling arguments) that describe the enhanced density fluctuations of flowing polymer solutions, and Rangel-Nafaile et al.²³ have presented an alternative approach for shear-induced "phase separation" based on thermodynamic arguments. More recently, Douglas has discussed²⁴ some of these issues. However, none of these models predicts an isotropic scattering pattern (as was observed in our experiments) because these were developed for low- Q (light) scattering.

Conclusions

We have examined the phenomenon of shear-induced turbidity in a solution of 3% deuterated polystyrene and DOP by small-angle neutron scattering. Above a critical shear rate, $I(Q=0)$ increases with increasing shear rate. For all shear rates examined, the scattering was isotropic. Using the RPA theory to fit the data, values of the polymer-solvent effective interaction parameter χ_{ps} (and of the segment length b) were determined as a function of shear rate. Values of the critical shear rate determined by SANS compare favorably with previous determinations using light scattering or turbidity measurements. The analysis of our data is based on the use of the RPA theory (its validity may be questionable in polymer solutions) and assumes that shear effects are contained only in χ_{ps} . The fact that isotropic SANS patterns were observed even at the highest shear rates is not understood. Because of the high molecular weight used, our observation range corresponds to chain portions ($QR_g > 1$) rather than whole chains. Radii of gyration are estimated to be around 35–45 nm and correlation lengths around 16 nm for the zero-shear case.

Acknowledgment. We acknowledge useful discussions with Drs. R. Briber, J. Douglas, A. Z. Akcasu, and M. Muthukumar. Allocation of beam time on the NIST NG7 30-m SANS instrument is greatly appreciated.

References and Notes

- (1) VerStrate, G.; Philippoff, W. *J. Polym. Sci., Polym. Lett. Ed.* 1974, 12, 267.
- (2) Hoshimoto, T.; Fujioka, K. *J. Phys. Soc. Jpn.* 1991, 60, 356.
- (3) Silberberg, A.; Kuhn, W. *Nature* 1952, 170, 450.
- (4) Kramer-Lucas, H.; Schenck, H.; Wolf, B. A. *Makromol. Chem.* 1988, 189, 1613.
- (5) Nakatani, A. I.; Kim, H.; Takahashi, Y.; Matsushita, Y.; Takano, A.; Bauer, B. J.; Han, C. C. *J. Chem. Phys.* 1990, 93, 795.
- (6) De Gennes, P.-G. *J. Phys. (Paris)* 1970, 31, 235.
- (7) De Gennes, P.-G. *J. Chem. Phys.* 1980, 72, 4756.
- (8) Shibayama, M.; Yang, H.; Stein, R. S.; Han, C. C. *Macromolecules* 1985, 18, 2179.
- (9) Han, C. C.; Bauer, B. J.; Clark, J. C.; Muroga, Y.; Matsushita, Y.; Okada, M.; Tran-Cong, Q.; Chang, T. *Polymer* 1988, 29, 2002.
- (10) Bates, F. S.; Wignall, G. D. *Phys. Rev. Lett.* 1986, 57, 1429.
- (11) Sakurai, S.; Hasegawa, H.; Hashimoto, T.; Hargis, I. G.; Aggarwal, S. L.; Han, C. C. *Macromolecules* 1990, 23, 451.
- (12) Trask, C. A.; Roland, C. M. *Macromolecules* 1989, 22, 256.
- (13) Zimm, B. *J. Chem. Phys.* 1948, 14, 164; 1946, 16, 1093.
- (14) Benoit, H.; Benmouna, M. *Polymer* 1984, 25, 1059 and 2468.
- (15) Helfand, E.; Fredrickson, G. H. *Phys. Rev. Lett.* 1989, 62, 2468.
- (16) Onuki, A. *Phys. Rev. Lett.* 1989, 62, 2472.
- (17) Milner, S. T. *Phys. Rev. Lett.* 1991, 66, 1478.
- (18) Certain equipment and instruments or materials are identified in this paper in order to adequately specify the experimental conditions. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that the materials are necessarily the best available for the purpose.
- (19) Nakatani, A. I.; Kim, H.; Han, C. C. *J. Res. Natl. Inst. Stand. Technol.* 1990, 95, 7.
- (20) Peterlin, A. *J. Chem. Phys.* 1955, 23, 2462.
- (21) Linder, P.; Oberthur, R. C. *Colloid Polym. Sci.* 1988, 266, 886.
- (22) Pistor, N.; Binder, K. *Colloid Polym. Sci.* 1988, 266, 132.
- (23) Rangel-Nafaile, C.; Metzner, A. B.; Wissbrun, K. F. *Macromolecules* 1984, 17, 1187.
- (24) Douglas, J. F. *Macromolecules* 1992, 25, 1468.

Registry No. PS (homopolymer), 9003-53-6; DOP, 117-81-7.