Table IX
Possibilities of Motions According to the Energy Change

Energy diff	Conf probability, %	Probability of motion, %[a]	% motion/ simulation cycle
$-2E_1$	0.85	72.6	0.61
$-E_1$	5.44	61.9	3.37
0	11.66	50	5.83
E_1	9.35	38.1	3.56
$2E_1$	2.49	27.5	0.68
Total	29.79	47.19	14.06

[a] See eq 1.

Table X
Influence of Blocked Conformations

Type of conf	A = conf probability, %	B = probability of the conf able to move	B/A
tgt	15.01	9.01	0.60
tgg	22.05	14.75	0.67
ggg	8.10	6.04	0.75
Total	45.16	29.80	0.66

formations which would have given the sterically forbidden conformation g^+g^-. But these cases were accounted for in the simulation as rejected by energy condition. In Table X, we reintroduce the probabilities of such conformations and obtain a correction factor of 0.66.

Incidentally, we observe that the conformations whose three-bond motions are favored are ggg, tgg, and tgt in decreasing order. We have already found that the simulation seems to favor slightly the conformations themselves in the same order. So it is possible that the simulation process tends to enrich the chains in the conformations which are most able to move. However, this effect is very small. Finally the efficiency of the simulation, defined as the ratio of performed motions/tentative motions, amounts to 31.1% by the above calculation, as compared with 32.3% by the simulation.

The ratio (number of motions/cycle of the simulation) is 14.1% (calculated) or 14.6% (simulation). This value is close to the 14.8% one obtains for a tetrahedral lattice chain without energy weighting.

Conclusion

We have tested the model developed in the simulation of chain Brownian motion by using the rotational isomer theory. A straightforward application to the polyethylene chain allowed us to show the consistency of the model with respect to conformational properties and even to local dynamic behavior. A similar analysis could have been done for any of the polyethers we have studied, but the complexity of the chain backbone would have made the calculations far more tedious, and the final conclusions would have been expected to be the same. The agreement between these two quite different approaches to conformational properties gives strong support to the simulation model.

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Verification of the Long-Range and Localized Dynamics of Molecules in an Amorphous Polymer Matrix

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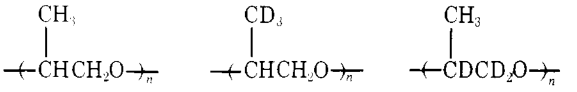
ABSTRACT: The neutron incoherent quasi-elastic scatter from polypropylene oxide certainly shows two quasi-elastic components, one in the rubber and the second in the glass below 200 K. Overall the dependence of broadening on momentum transfer is consistent with the origin of the high-temperature component as local main chain wriggling and the low-temperature component from hindered internal rotation of the methyl group. Although the effects observed demonstrate the qualitative aspects of the rotational isomeric model, better experimental results are required at low temperatures to enable the scattering law and the activation energy for methyl group rotation to be evaluated with precision comparable to that achieved in the measurement of torsional frequencies.

Molecular theories of polymerized materials are based on the rotational isomeric model.[1] An individual chain is built up of a series of small repeat units, the geometry of each unit being essentially that of the corresponding small molecule. The backbone of the polymer chain is a sequence of σ bonds, sometimes interspersed by bonds of higher order, and the backbone subtends atoms or side groups to make up the complete macromolecule. In the crystalline state, the model chain can assume a planar zig-zag form (achieved for example by a sequence of trans rotational conformers about the σ bonds in a carbon–carbon or carbon–oxygen chain) or a regular helical form (which requires, for example, a specific sequence of gauche rotational conformation about main σ chain bonds). In amorphous states more random conformations are required. The model satisfies this requirement by internal rotations about the main chain bonds, which are correlated over only very short sequences of bonds or virtually independent. Thus, for a given chain millions of rotation isomers are generated and the chain is usually specified in terms of the average of the radius of gyration or end-to-end distance for this total set of isomers rather than by the specification of each individual isomer. The side groups also undergo internal rotations about σ bonds joining them to the main chain and if long enough they too can enjoy a series of conformations.

Now consider the application of the rotational isomeric model to the amorphous states of polymerized matter. In solution each polymer molecule undergoes center-of-mass diffusion, but in addition internal rotation about main chain bonds is rapid and each molecule is continually exploring all the rotational isomers available. The side groups also rotate. In the rubbery state, center-of-mass diffusion is very slow indeed and is ignored except for particular phenomena such as creep. However, internal rotation is still rapid and all rotational isomers of the chain are involved in the contortions of each chain. In the glass the conformational flexibility of each chain disappears. Each chain is frozen into one of its rotational isomers and the matrix is considered to be an assembly of irregularly packed chains involving a very wide range of the rotational isomers possible. This transformation from wriggling to frozen chains occurs in the glass transition region but through this region the side groups continue to rotate and they are frozen in at lower temperatures.

Direct verification of this model can be obtained from quasi-elastic incoherent neutron scattering studies over a suitably wide range of temperature. The key to the unambiguous assignment lies in the different scattering laws which are predicted for the local main chain wriggling motion that develops from internal rotational motions about main chain bonds and for the rotational motion of simple side groups such as CH_3 or C_6H_5 about fixed lattice sites as is supposed to be the case in the glassy state.

A suitable polymer for such a study is polypropylene oxide, not only because its chemical structure should generate the required effects but also because the quasi-elastic broadening arising from the methyl group can be determined explicitly by comparing the scatter from the isotopic species.



$$-\!\!\left(\underset{}{\overset{CH_3}{\overset{|}{C}}}HCH_2O\right)\!\!-_n \qquad -\!\!\left(\overset{CD_3}{\overset{|}{C}}HCH_2O\right)\!\!-_n \qquad -\!\!\left(\overset{CH_3}{\overset{|}{C}}DCD_2O\right)\!\!-_n$$

The quasi-elastic incoherent scattering law for the main-chain motion is of the form[2]

$$S_{\text{incoh}}(Q,\omega) \tag{1}$$

$$S_{\text{incoh}}(Q,\omega) \equiv \frac{1}{2\pi n} \int \langle \sum_n e^{-iQ\cdot(R_n(t) - R_n(0))} \rangle \, e^{i\omega t} \, dt \tag{2}$$

where R_n are the coordinates of the nth subunit in the chain at times zero and t. Q and $\hbar\omega$ are respectively the momentum transfer and energy transfer in the scattering process.

If we assume that the motion is essentially Gaussian, the expression simplifies to:

$$S_{\text{incoh}}(Q,\omega) = \frac{1}{2\pi} \int e^{-(Q^2/6)\langle (R(t)-R(0))^2 \rangle} e^{i\omega t} \, dt \tag{3}$$

where R is now the coordinate of a typical subunit of the chain. The form of the time correlation function is obtained from the Langevin equation using a Rouse[3] or Zimm[4] model. For the Brownian motion of a simple point in a chain, constrained in its motion by its attachment to its neighboring units, the time correlation function is

$$\langle (R(t) - R(0))^2 \rangle \propto t^{\alpha} \tag{4}$$

For the Rouse model $\alpha = 1/2$ and for the Zimm model $\alpha = 2/3$. The corresponding quasi-elastic scattering laws are characterized by widths at half full height which are proportional to Q^4 and Q^3, respectively. Thus the broadening of the quasi-elastic scatter is strongly dependent on the angle of scatter since $Q = (4\pi \sin \theta/2)/\lambda$.

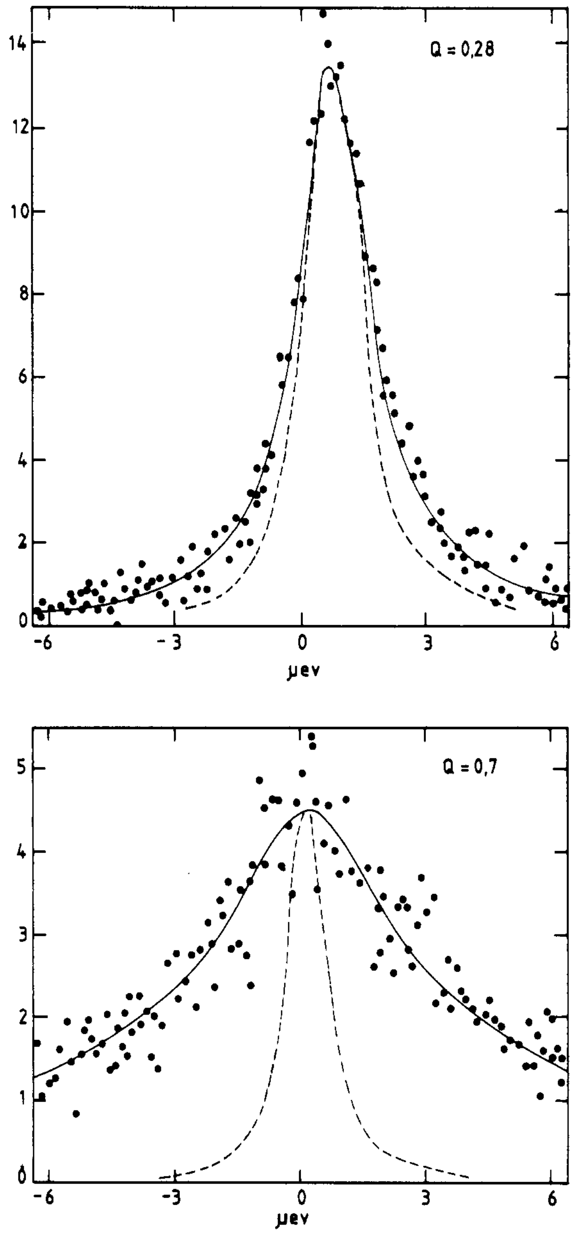


Figure 1. $S(Q,\omega)$ for polypropylene oxide at 340 K; $Q = 0.28$ and 0.70 Å^{-1}. The solid lines are the best fit of the Rouse model to the data (instrumental resolution has been included). The broken lines are the instrumental resolution itself.

For a symmetric top such as a methyl group rotating about a fixed lattice site in a series of jumps between equivalent positions the scattering law is predicted to be of the form:

$$S(Q,\omega) = A_0(Q)\delta\omega + \frac{1}{\pi}(1 - A_0(Q)) \cdot \frac{2\tau/3}{1 + \omega^2(2\tau/3)^2} \tag{5}$$

A_0 is a form factor which is governed by the area swept out by the scattering nuclei (in this case three protons) of the rotating methyl groups. In fact

$$A_0(Q) = \tfrac{1}{3}\,(1 + 2j_0(Qa(3)^{1/2})) \tag{6}$$

where a is the radius of the sphere or circle on which the scattering nuclei move. j_0 is the zero-order spherical Bessel function and τ is the mean time between two successive jumps. The structure of the quasi-elastic peak contains a central δ

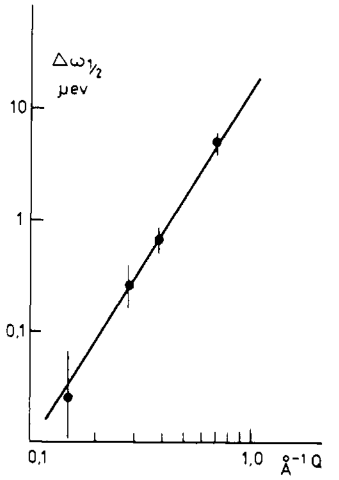
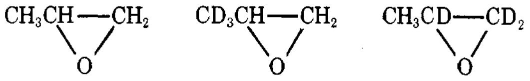


Figure 2. Full width at half maximum, $\Delta\omega_{1/2}$, of $S(Q,\omega)$ against Q for the data of Figure 1. Double logarithmic plot.

function (which does not appear in the quasi-elastic scatter from main chain motions) which arises from the essentially fixed center-of-mass of the scattering group and a quasi-elastic component whose breadth is *independent* of momentum transfer but which has a full width at half maximum height of $^1/\tau$. The jump time τ between rotational sites is, of course, a function of temperature. It is possible to use other more complex models for the motion but they will always share the common factor of an unbroadened and a broadened component.

Experimental Section

Materials. Amorphous polypropylene oxide samples were made from the three monomers



using a zinc diethyl/water catalyst. The samples were kindly made by Dr. R. O. Colclough. $M_w = 1.1 \times 10^6$ and $M_w/M_n \sim 4$.

Neutron Scattering. The quasi-elastic spectra were obtained using the IN10 back-scattering instrument at the Institut Laue-Langevin at Grenoble.[6] The sample, in the form of a thin film pressed between aluminum foil, was mounted perpendicular to the neutron beam. The wavelength of the neutrons was 6.28 Å and the instrument has a 1 μeV resolution at the full width of half peak height.

Data Analysis. In the high-temperature experiments, the full width at half peak height ($\Delta\omega_{1/2}$) of the scattering law $S(Q,\omega)$ is of the order of the resolution function. Values of $S(Q,\omega)$ predicted by the models are convoluted with the resolution function of the spectrometer and the results were fitted to the experimental data.

In the low-temperature data the broadening is again only of the order of a few μeV. The relatively intense elastic component with its Lorenztian line shape (the line shape of the instrumental resolution itself) makes separation of the broadened component due to methyl rotation difficult. Again it is necessary to calculate the whole form of

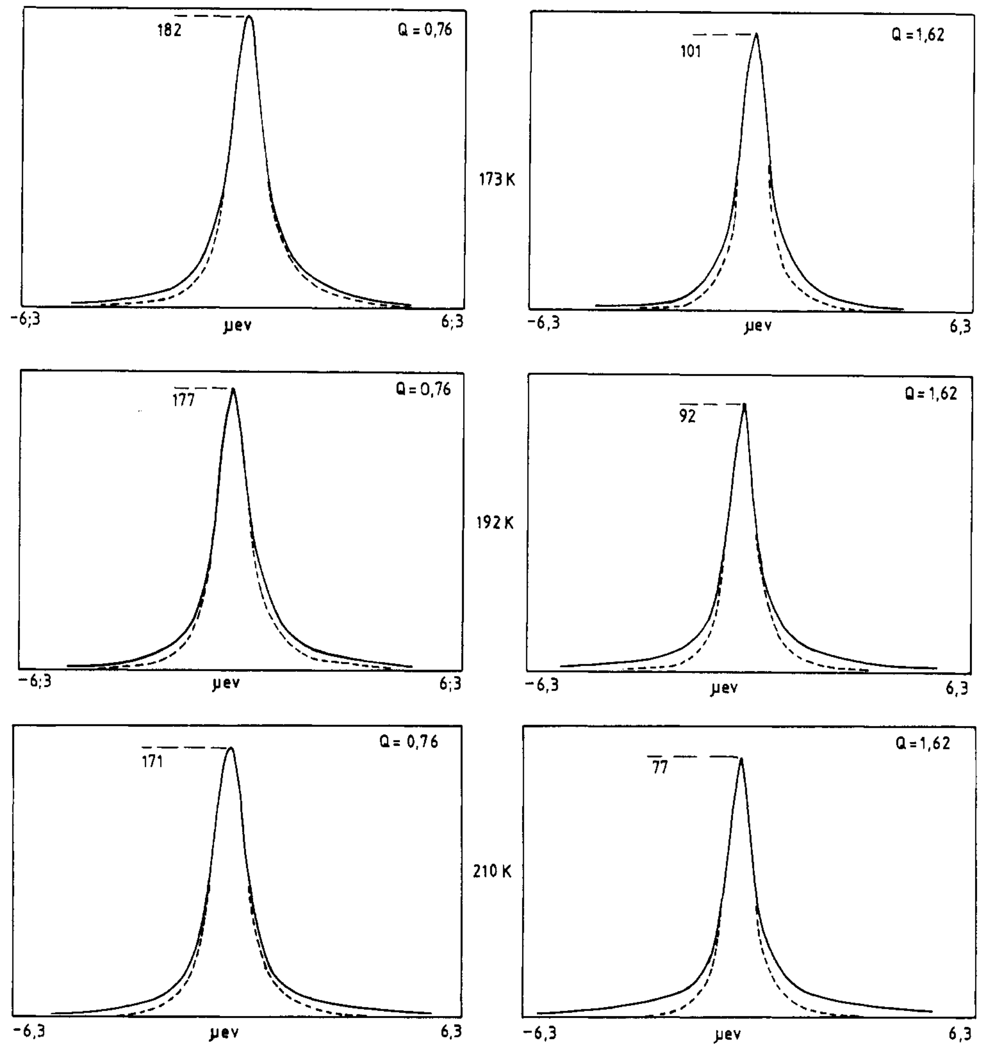


Figure 3. Quasi-elastic scattering from PPO at two values of momentum transfer Q and three temperatures. Broadening increases in intensity with Q and in magnitude with T. The broken line is the instrument resolution function in each scattering angle. Note the peak height decreases with increasing Q indicating the transfer of intensity from elastic to inelastic components (cf. eq 5 and 6).

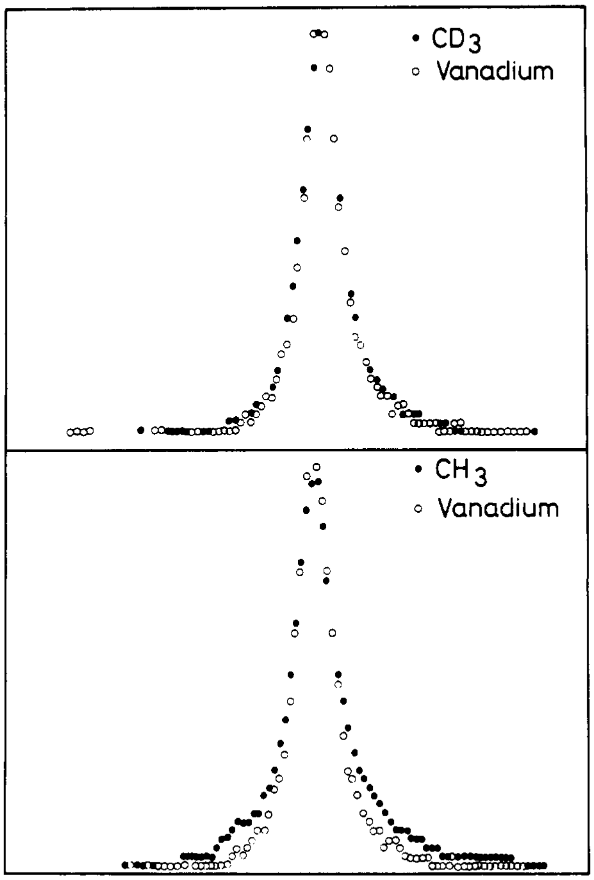


Figure 4. Comparison of the quasi-elastic scattering from polypropylene oxide $\text{-(}CD_2\text{-}C(CH_3)D\text{-}O\text{-)}_n$ and $\text{-(}CH_2\text{-}C(CD_3)H\text{-}O\text{-)}_n$ (●) at 173 K and Q = 1.62. Also shown is the instrumental resolution represented as the scattering from vanadium (○).

eq 5, convolute it with the resolution function, and fit these curves to the experimental data. Some details of the choice of parameters are given in the discussion.

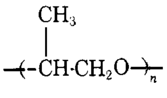
Results

At 340 K the quasi-elastic scattering proved to be a strong function of momentum transfer and at each angle of scatter to consist of one broad smooth component. In a detailed investigation of the quasi-elastic scattering from polymers at high temperatures[7,8] it was shown that a model of the scattering law based on the Rouse model provided a good fit to the data.

In Figure 1 $S(Q,\omega)$ data for polypropylene oxide at 340 K are shown for two values of the momentum transfer Q. The solid lines are the result of the best fit to these data of the fourier transform of eq 3 (using the time correlation in eq 4 and $\alpha = \frac{1}{2}$) convoluted with the instrumental resolution.

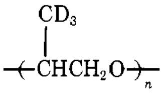
Figure 2 shows the half-widths of the best fit $S(Q,\omega)$ against Q on a double logarithmic plot. Although for conciseness we here discuss only high resolution low Q data the results in Figure 2 have been extended over a wider range of Q using two other instruments.[8] The line drawn in Figure 2 has a slope of 3.1. The Rouse model actually predicts $\Delta\omega_{1/2}\alpha Q^4$ and deviations from the fourth power behavior seen for most polymers in this Q range are discussed in full in ref 7 and 8. As the temperature is raised the exponent of Q increases toward the value 4.

In a previous study[9] in which the quasi-elastic scatter from



$$\text{-(}\underset{\displaystyle |}{\overset{CH_3}{}}\!CH\text{-}CH_2O\text{-)}_n$$

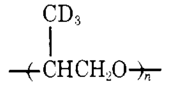
and



$$\text{-(}\overset{CD_3}{CH}CH_2O\text{-)}_n$$

were compared it was shown that this high-temperature broadening originates from the main chain only. As the temperature of the sample is reduced the quasi-elastic broadening reduces and at about room temperature becomes unmeasurably small. Until close to 200 K, the glass transition of polypropylene oxide, there is no detectable broadening of the elastic peak.

In the glass, a second type of quasi-elastic broadening is detected at 200 K and below, but this has a different structure from that of the high-temperature broadening. Now the broadening appears as symmetrical wings attached to an unbroadened central component. The broadening is substantially independent of Q as can be seen in Figure 3, but the width of the quasi-elastic wings is a function of temperature. Figure 4 shows conclusively that the methyl group is the origin of the quasi-elastic broadening observed at low temperatures since it is not observed in the



$$\text{-(}\overset{CD_3}{CH}CH_2O\text{-)}_n$$

sample.

Discussion

These and previous results demonstrate that the quasi-elastic broadening observed above room temperature originates from main chain motion and furthermore has the expected dependence on momentum transfer of full width at half maximum height of

$$\Delta\omega_{1/2} \propto Q^3 \rightarrow Q^4$$

Below the glass transition the quasi-elastic broadening due to methyl group rotation is at first too broad to be detected but as τ reduces with temperature it is ultimately detected at about 200 K. The quasi-elastic scatter displays the two-component behavior predicted by theory and its width is not very strongly dependent on Q, the momentum transfer.

Finally, it is possible to extract from these results values of τ as a function of temperature and hence to estimate the activation energy for methyl group rotation in polypropylene oxide. In practice this is difficult because the statistics are barely adequate for the curve-fitting procedures and in our particular case because of the Lorentzian instrumental resolution function.

For a methyl group rotation the form of $A_0(Q)$ is well known.[5] It is also known that for this model τ should not vary with Q but only with temperature. Because of the difficulties mentioned above it is desirable to reduce the number of variables in the fitting procedure to a minimum.

The theoretical values of $A_0(Q)$ were fed into the program and the best fit value of τ which was constant over all the Q values was obtained at each temperature. The temperature dependence of τ corresponds to an activation energy of 17 K J mol^{-1}.

This result is in reasonable agreement with the previously determined value[10] of V_3 of 14.7 K J mol^{-1} obtained from the methyl group fundamental torsion. Better experimental results are now required so that τ may be determined with the same precision as the torsional frequency. Comparison of this activation energy with V_3 may then lead to more detailed information on the shape of the potential barrier for methyl rotation.

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Viscometric Determination of Thermodynamic Demixing Data for Polymer Solutions†

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ABSTRACT: Viscosity coefficients η were determined for the two systems cyclohexane/polystyrene ($M = 390\,000$) and *trans*-decahydronaphthalene/polystyrene ($M = 110\,000$) both of which exhibit upper critical solutions temperatures. Measurements were performed in the concentration range 3 to 15 wt % polymer and at shear rates from 40 to 1400 s^{-1}. Plots of η vs. T fall into two parts separated by a sharp discontinuity, which coincides with the visually determined cloud points within ±0.1 K. On evaluation of the homogeneous part of the different isopleths, a minimum in the apparent activation energy of flow is found at half the critical composition, in addition to the well-known maximum at the consolute point. Within the two-phase region reproducible measurements can be performed down to a few degrees below the demixing temperature. The amount of breakdown of the viscosity upon entry into the two-phase region is highly concentration dependent. It is most pronounced for the critical composition, and thus constitutes a new method for determination of critical conditions. Plots of log η vs. wt % polymer are practically linear sufficiently far from the critical temperature. Additional contributions in the neighborhood of the critical composition appear when the critical temperature is approached.

A great number of physical properties of binary liquid mixtures show certain peculiarities near their consolute point. Among them are: heat capacity,[1] ultrasonic absorption,[2] light scattering,[3] sedimentation,[4] and viscosity.[5-7] The present work evolved from our measurements on the excess viscosity of polymer solutions exhibiting both upper and lower critical solution temperatures.[8] In the course of this investigation we have observed a rapid breakdown of the viscosity of the homogeneous polymer solutions when the low-temperature demixing sets in. It was therefore near at hand to check whether this effect could be utilized to determine demixing temperatures. Such a method would be of particular interest for systems for which a visual determination of the cloud-point temperature is impossible (i.e., isorefractive components, colored solutions, or systems enclosed in windowless cells). Two further goals of the present investigation were the extension of the viscosity measurements into the two-phase region and the examination of the existence of viscometric critical concentrations[9] in the solutions under consideration.

Experimental Section

Apparatus. Viscosity measurements were carried out on the "Rotationsviskosimeter RV 2″ and its attachments as supplied by Haake Messtechnik OHG, using the sensor system NV (cup and bell shaped rotor). By means of the measuring heads MK 50 and MK 500, differing in their maximum torque, viscosity coefficients can be measured in the range from 5 to 10^5 mPa s, the shear rate D running from 10 to 5400 s^{-1}.

Materials. Two samples of polystyrene with the nominal molecular weights 110 000 and 390 000, obtained from the Pressure Chemical Co., were investigated. The values 0.06 and 0.1, respectively, are given by the producers for the molecular nonuniformity ($(M_w/M_n) - 1$). Cyclohexane (p.a.) and *trans*-decahydronaphthaline (zur Synthese) were obtained from E. Merck, Darmstadt. The former solvent was used without further treatment, whereas the latter was carefully redistilled in a silver-mantel column.

Viscosity Measurements. The solvent/polymer systems were kept at 40 to 50 °C for 1 week and were stirred from time to time in order to guarantee thermodynamic equilibrium. Viscosity measurements were then carried out at various temperatures, which have been reached by slowly cooling the solutions (less than 0.5 °C/h). Within the two-phase region the viscosity coefficient η can be determined reproducibly as long as the distance to the demixing temperature does not exceed a few degrees. In the case of cyclohexane, the normally open lower part of the apparatus containing the solution was sealed by means of steel cuffs in order to prevent losses of the solvent due to evaporation. The η values for the different velocity gradients were determined point by point; in addition some rheograms were also taken.

Results and Discussion

For a given solvent/polymer system and fixed molecular weight of the polymer, the viscosity coefficient depends on concentration, temperature ($p = 1$ bar), and shear rate D. In context with out present investigation, a potential non-Newtonian behavior of the polymer solution would only be a complicating side effect. For this reason we have looked for conditions under which η is independent of D.

Shear Rate Dependence. Figure 1 gives the results for the system cyclohexane/polystyrene ($M = 390\,000$) and the indicated temperatures. For the lower molecular weight polystyrene in *trans*-decahydronaphthaline, no non-Newtonian behavior can be observed within the range of shear rates experimentally accessible with our apparatus. The "upturn effect" shown in Figure 1, which has already been reported in the literature,[10] will not be discussed here; the only conclusion we draw is that we are positively outside the non-Newtonian region at $D = 1000$ s^{-1} and that the non-Newtonian behavior observed at low D values vanishes as the demixing conditions are approached.

Temperature Dependence. An example for the variation of η with temperature can be seen in Figure 2 for cyclohex-

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† Dedicated to Professor M. L. Huggins in honor of his 80th birthday.