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Degradation of Chain Molecules. 2. Thermodynamically Induced Shear Degradation of Dissolved Polystyrene

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ABSTRACT: The degradation of polystyrene ($2.60 \times 10^3 \leq P_n \leq 1.50 \times 10^4$) in semiconcentrated solutions (4.9–20 wt %) in *trans*-decalin (Θ solvent) has been studied at moderate shear rates (laminar flow, $5 \times 10^3 \leq \dot{\gamma} \leq 10^4$ s^{-1}). The results demonstrate that the scission of the C–C bonds is induced by the poor solvent quality. The breakage of chains leads to radical fragments that either recombine or react with added radical scavengers. Special attention has to be paid to the choice of the radical scavengers in order to avoid changes in solvent quality. The rate of degradation increases strongly with concentration. The breakage probability evaluated on the basis of the method described in part 1[1] is Gaussian along the chain. The standard deviation, expressed by the parameter R, amounts in most of the cases to 10–15% of the actual chain length. The exponent X describing the dependence of the rate of degradation on the individual chain length is comparatively small (0.1–0.9) and depends on temperature and shear rate. Since the effect is thermodynamically induced, the influence of temperature is very pronounced. All findings are compared to recent viscosimetric results[2] and can be explained in terms of the modified Graessley theory.[2,3]

Introduction

In the first paper of this series[1] the kinetic scheme describing the degradation process of chain molecules was solved exactly. It was demonstrated that each model of interest can be treated by this procedure. Thus the individual rate constants $k_{i,j}$ for the scission of a chain of length i into two fragments with j and $i - j$ subunits respectively can be obtained by fitting different models to experimental distributions. These rate constants $k_{i,j}$, i.e., the breakage probability as a function of chain length i and position of the jth bonds, clearly reflect the stress along the chain. This information is not available by any other method. Thus degradation experiments under suitable conditions can be used as a tool for studying special aspects of chain dynamics in a sheared liquid. In order to connect the kinetic data obtained by the above method with external forces applied to the molecules, the degradation experiment has to be carried out under laminar conditions; i.e., the acting shear rate must be well defined. But in many cases[4] the shear rate to be applied to cause the scission of the C–C bonds is of the order of 10^5 s^{-1}. Thus the degradation can be observed very often only under turbulent conditions. Some years ago it was observed[5] that polystyrene is degraded even at moderate shear rates (10^3–10^4 s^{-1}) when dissolved in a Θ solvent, whereas no scission occurs under the same conditions in a good solvent. This effect provides convenient access to degradation under laminar conditions. In this paper this "thermodynamically induced shear degradation" is studied with respect to molecular weight distribution, solvent quality, concentration, and shear rate. Since the scission of the C–C bond is homolytic, special attention is paid to the influence of added radical scavengers such as oxygen or DPPH (2,2-diphenyl-1-picrylhydrazyl). The results are compared to recent viscosimetric results,[3] leading to a semiquantitative understanding of the degradation process in terms of the modified Graessley theory.[2]

Experimental Section

Materials. Toluene, analytical grade (Merck, Darmstadt), was used without further purification. *trans*-Decalin (Merck-Schuchardt) was carefully fractionated before use. The final content of the cis isomer as checked by gas chromatography amounts to less than 0.2%. DPPH (Fluka, purum) was used without further purification. Solubility data of oxygen in *trans*-decalin, necessary for comparing the influence of different radical scavengers are not available from the literature but can be estimated from data of similar hydrocarbons to be ca. 0.1 cm^3 of O$_2$/cm^3 of solvent at 1 atm. This corresponds to a concentration of 4.5×10^{-3} mol/L.

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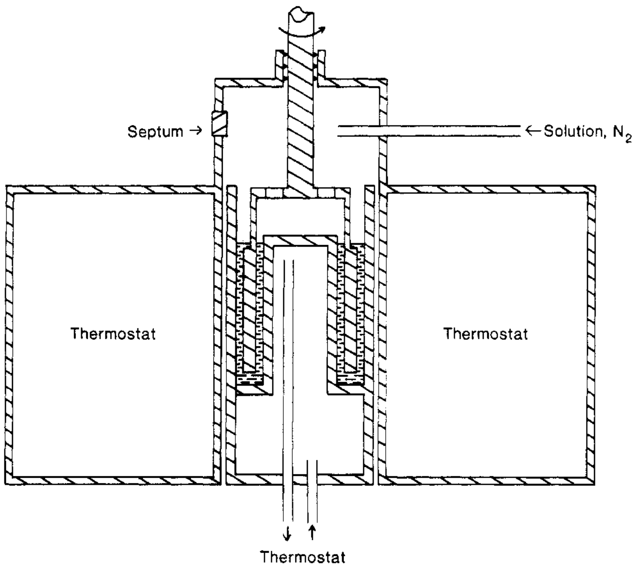

Figure 1. Shearing device (see text for data).

For the sake of a meaningful comparison the concentration of DPPH was adjusted to the same value (corresponding to 1.75 mg/cm^3) when this radical scavenger was used. Comparing the maximum number of broken bonds per chain (see below) to the number of radical scavenger molecules per chain shows that the latter is higher by a factor of approximately 10. This ensures that the concentration of the radical scavengers can be regarded as constant throughout the reaction.

Polystyrene samples with a broad molecule weight distribution were obtained by thermal polymerization at 62 °C.[7] Their data are (1) $P_w = 1.52 \times 10^4$, $P_w/P_n = 1.7$; and (2) $P_w = 1.70 \times 10^4$, $P_w/P_n = 1.7$, with P_w and P_n being the weight- and the number-average degree of polymerization (determined by gel permeation chromatography).

Three narrowly distributed polystyrene samples were prepared anionically by means of the break seal technique.[8] The respective data are (1) $P_w = 1.80 \times 10^4$, $P_w/P_n = 1.2$; (2) $P_w = 6.70 \times 10^3$, $P_w/P_n = 1.1$; and (3) $P_w = 2.80 \times 10^3$, $P_w/P_n = 1.06$. Because of the large amounts of monomer (ca. 30 g) used for the polymerization runs, the mixing time of the monomer with the initiator solution is comparatively long. The molecular weight distribution is therefore broader than expected for anionically polymerized samples (cf. ref 8). Since the evaluation of the $k_{i,j}$ as outlined in part 1 does not assume monodisperse samples but can be applied to any type of distribution, this effect does not invalidate the results. All solutions were homogenized by stirring for at least 48 h. For experiments in the presence of oxygen, the solvent was saturated with O_2 before the polymer sample was dissolved.

A thorough discussion of the thermodynamics of the system *trans*-decalin/polystyrene has been given recently.[9] Cloud point temperatures have been determined visually. Unfortunately, the dark color of the solutions containing DPPH prevents a determination of the point of phase transition by optical means. Therefore alterations effected by DPPH on the solvent quality (see below) cannot be studied directly.

Apparatus and Procedure. Shear Cell. As already mentioned the experiments must be carried out under laminar conditions. This has been achieved by a Couette-type apparatus consisting of a bell-shaped rotor and a well-thermostated stator (see Figure 1). The rotor has inner radius 17.85 mm, outer radius 20.10 mm, and length 60 mm, and the stator has inner radius 17.5 mm and outer radius 20.5 mm. The width of the inner gap is slightly smaller than that of the outer, ensurring the same shear rate in both gaps.

For studying the influence of radical scavengers, both filling and running the experiments are done under an inert-gas atmosphere. Samples of the solution are taken directly above the outer gap by means of a syringe inserted through the septum (see Figure 1). In addition to this, control experiments were made by taking the whole solution as a probe. This leads to the same result, which demonstrates that there is a sufficiently fast exchange of the liquid in the gap and that in the volume below the rotor (cf. Figure 1); i.e., this volume in which the liquid is not sheared does not disturb the measurements under the present experimental conditions.

For the device outlined above the viscosities of the polymer solution under consideration, and Reynolds number is of the order of 10, so the flow conditions are laminar. Since in the outer gap the velocity of the fluid particles near the rotating inner cylinder is higher compared to that near the stator, the flow may become unstable and produce Taylor vortices when the speed is high enough. The criterion for this flow instability is given by the Taylor number, *Ta*,[10] which should be less than 41.3:

$$Ta = \frac{\omega R_i(R_a - R_i)}{\nu}[(R_a - R_i)/R_i]^{1/2} < 41.3 \tag{1}$$

where ν is the kinematic viscosity, $\omega = 2\pi n$, n is the number of revolutions, and R_i and R_a are the inner and outer radius, respectively. For the present conditions Ta is approximately unity. Thus the flow can be regarded as stable.

Another problem could result from the highly non-Newtonian behavior of the semiconcentrated polymer solutions. In the region of shear where degradation takes place the viscosity is well represented by a power law:[3]

$$\eta \sim \dot{\gamma}^{m-1} \tag{2}$$

where $\dot{\gamma}$ is the shear rate. The mean value of the shear rate in the gap, which for Newtonian fluids is[11]

$$\langle\dot{\gamma}\rangle = 2\omega R_i R_a/(R_a^2 - R_i^2) \tag{3}$$

has to be corrected therefore to[11]

$$\dot{\gamma}_{\mathrm{corr}} = \langle\dot{\gamma}\rangle \frac{1 - (R_i/R_a)^{2s}}{s(1 - (R_i/R_a)^2)} = \langle\dot{\gamma}\rangle K \tag{4}$$

with $s = m^{-1}$. For solutions of polystyrene in *trans*-decalin m is given by 0.5,[3] which results in a negligible correction ($K = 0.99$). Solutions of polystyrene in toluene exhibit smaller values of m 0.2, ref 3). This leads to $K = 0.93$; the corrected shear rate is therefore 7% smaller than calculated by eq 3. This difference is appreciable but cannot explain the totally different sensitivity of the polymer chains toward degradation with respect to solvent power.

The most complicated problem caused by the high shear rates is the evolved heat due to the dissipation of energy. This might lead to a rise of temperature in the gap. An estimate of the effect can be obtained by the following calculation:

The energy dissipated per volume and time is given by

$$\dot{E}_v = \eta\dot{\gamma}^2 \tag{5}$$

Let $\dot{Q}$ denote the flux of heat; then[12]

$$d\dot{Q} = \alpha\, dF\, \Delta T \tag{6}$$

where F is the area and α is the coefficient of thermal conduction. From the balance of energy,[12,13] ΔT becomes

$$\Delta T = (d\dot{Q}/dF)(1/\alpha_d + \delta/\lambda_{ST} + 1/\alpha_w) \tag{7}$$

where α_d is the coefficient of thermal conduction from the solution inside the gap to the stator, δ is the thickness of the stator, λ_{ST} is the heat conductivity of steel, and α_w is the coefficient of thermal conduction applying to the heat transfer from the stator to the thermostated water (cf. Figure 1). α_w can be roughly estimated for the equipment under consideration as 2×10^3 J m^{-2} s^{-1} K^{-1}.[11,14] The coefficient of thermal conduction for organic liquids is usually smaller than that measured for water,[12] but taking into account the high mean velocity in the gap makes a value of α_d on the order of magnitude of α_w more probable.[14] With $\delta = 2 \times 10^{-3}$ m, $\lambda_{ST} = 46.5$ J m^{-1} s^{-1} K^{-1} (see ref 6), $\dot{Q} = \eta\dot{\gamma}^2 V$ (V is the volume inside the gap), and $\eta = 0.1$ Pa s (at typical shear rates), ΔT is estimated to be 1–3 K. The calculation shows that the rise of temperature in the gap may be considerable. But it does not take into account that there is a fast exchange of the liquid in the gap and the volume below the rotor (cf. Figure 1 and see above). This certainly will diminish such a temperature gradient. Furthermore, an uncertainty in determining the temperature in the system only would disturb the comparison of experiments done at different shear rates. Clearly, a smaller width of the gap would diminish the problem but increase the volume outside the gap in comparison to the volume inside the gap. Thus, only a very small part of the solution would be sheared. With such a device, the simple and reliable method of taking samples of the solution during the degradation experiment (see above) would no longer be applicable or would lead to serious errors. Therefore, the equipment as described above seems to be more suitable for the degradation experiments.

GPC. The molecular weight distribution of the samples was obtained by a high-pressure gel permeation chromatograph (Waters, 4 Styragel columns (two 10^6-Å columns, one 10^5-Å column, one 10^4-Å column); solvent, tetrahydrofuran; UV detection). The axial dispersion of the columns was checked by the 4σ method of Wesslau[15] and found to be small compared to the molecular nonuniformity of the samples. Therefore, the mass fraction of the respective species was set directly proportional to the height of the eluogram divided by the slope (determined by a fit of a cubic polynomial) of the calibration curve. The exact solution, which involves the inversion of the corresponding integral equation,[16] is ill-conditioned and leads to oscillating solutions. Furthermore, the accuracy of the molecular weight distribution was controlled by analyzing polystyrene samples of known molecular weight distribution (thermally polymerized polystyrene[7]). The agreement is very satisfying and indicates that the error caused by neglecting the axial dispersion is within experimental uncertainty.

Kinetics. In order to evaluate the kinetic data we first define an overall rate of degradation as the number of broken bonds per molecule and time: With $B = (P_{n,0} - P_{n,t})/P_{n,t}$, the number of broken bonds per molecule,[1] the reaction rate is given by $\mathrm{d}B/\mathrm{d}t$ ($P_{n,0}$ and $P_{n,t}$ denote the number-average degrees of polymerization at $t = 0$ and t, respectively). In nearly all cases considered so far there is a maximum number of broken bonds depending on the experimental conditions which corresponds to the limiting degree of polymerization $P_{n,\infty}$:

$$B_\infty = P_{n,0}/P_{n,\infty} - 1 \tag{8}$$

The B vs. time curves are well represented by the equation[17,18]

$$\mathrm{d}B/\mathrm{d}t = k(B_\infty - B_t) \tag{9}$$

In some cases B_∞ could be obtained directly from the B vs. t plots; in most cases it was calculated by fitting it, together with k, to the data by means of a nonlinear fit procedure (see ref 3, Appendix). This furthermore provides convenient access to the initial rate of degradation:

$$(\mathrm{d}B/\mathrm{d}t)_{t=0} = kB_\infty \tag{10}$$

which turns out to be most useful for discussing the data.

To discuss the data in terms of the kinetic scheme elaborated in part 1[1], the experimental distributions of the original and the degraded samples were smoothed by a cubic polynomial. The vector $n(t)$ (cf. eq 4, part 1) then is given by the values of the smoothed experimental number distribution for a discrete set of equidistant molecular weights. All calculations discussed here were carried out by setting the number of chosen points to 50. This leads to different sizes of the breakage units (see part 1: 1000 for the highest molecular weight $P_w = 1.80 \times 10^4$, 150 for $P_w = 6.70 \times 10^3$, and 70 for $P_w = 2.80 \times 10^3$). By varying the size of these units it was ensured that the number of monomers per unit does not influence the results. Next the elements of the matrix **A** (eq 6, part 1) are calculated by means of the particular model under consideration. In the case of random or central scission the structure of **A** is very simple; for the model of Gaussian scission the $k_{i,j}$ have to be calculated for each set of X and R (eq 29, part 1) separately. The matrix **C** (eq 7 of part 1) then is determined by eq 15 of part 1, and introducing the number distribution at $t = 0$ leads to the coefficients α_i (eq 8a, part 1). The constant k (eq 23, 27, and 35 of part 1) now is varied until the sum S

$$S = \sum_j^{N_p} \sum_i^{50} (n_i^{\mathrm{calcd}}(t_j) - n_i^{\mathrm{exptl}}(t_j))^2 \tag{11}$$

where N_p is the number of samples taken, reaches a minimum. The whole calculation is repeated with another set of model parameters until the absolute minimum of S is obtained. In all cases, 5–8 experimental distributions of degraded samples were fitted by this procedure.

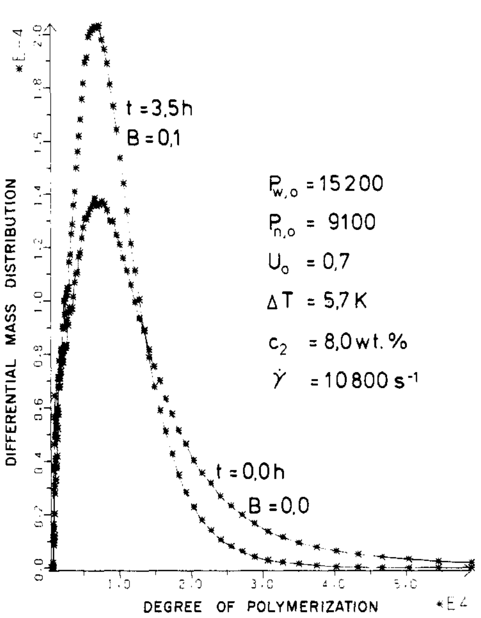

Figure 2. Comparison of the differential molecular weight distribution of a thermally obtained polystyrene before ($B = 0$) and after shearing in the absence of radical scavengers. U_0 denotes the molecular nonuniformity ($P_w/P_n - 1$) at $t = 0$, and ΔT is the distance to the actual demixing temperature.

Results and Discussion

General Considerations. A comparison between degradation experiments in the Θ solvent *trans*-decalin and the good solvent toluene again reveals (see ref 5) that the scission of chains only occurs in the poor solvent. This is not due to the difference in viscosity of the respective solutions. It has been shown[3] that this difference is large at low shear rates but much smaller (~40%) at shear rates applied for the degradation experiments under consideration. The difference in shear stress thus cannot account for the different behavior in both types of sovent. Therefore it can stated that the scission in the poor solvent is induced by the thermodynamic conditions. But it is not a critical phenomenon since it can be shown[3] that the critical effects only play a minor role in the range of concentration and temperature under consideration.

The scission of the C–C bonds is homolytic as expected for mechanical degradation in a nonpolar solvent. This has been proved by consumption of a stable free radical during the ultrasonic degradation of polystyrene.[18,19] Further insight into the mechanism of scission is provided by degradation experiments carried out with polystyrene samples of different molecular nonuniformity. When radical scavengers are excluded, the molecular weight distribution of a comparatively narrowly distributed polystyrene sample remains unaltered within experimental uncertainty. Carrying out the same experiment with a broadly distributed sample leads to a narrowing of the distribution (Figure 2). In this case the resulting change in P_n is small (ca. 6%/h) whereas P_w is lowered to a much greater extent (ca. 30%/h). This provides further evidence for the fact that the shearing forces split the chains into radical fragments which mostly recombine randomly in the absence of radical scavengers. Addition of oxygen or DPPH increases the rate of degradation as measured by $\mathrm{d}B/\mathrm{d}t$ (see eq 9) by more than 1 order of magnitude. As already mentioned the analysis of the molecular weight distribution of the degraded samples by the method described in part 1[1] is carried out more easily when the

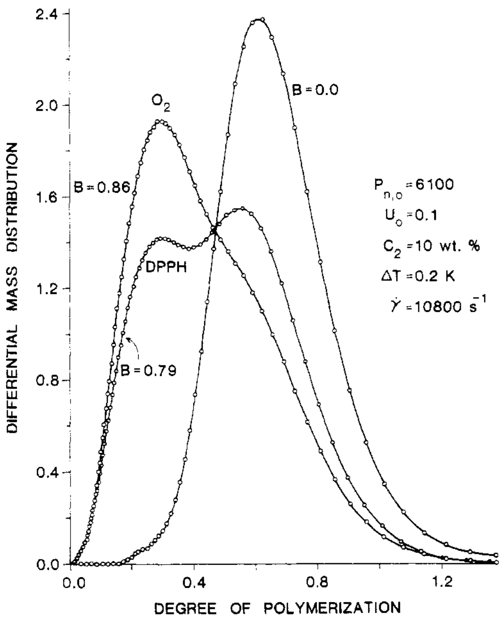

Figure 3. comparison of the starting distribution of an anionically obtained polystyrene (B = 0) and the distributions after 6 h of shearing the presence of oxygen and in the presence of DPPH. B denotes the number of broken bonds per chain (cf. part 1, eq 25), U_0 is the nonuniformity ($P_w/P_n - 1$) at t = 0, and ΔT is the distance to the actual demixing temperature.

distribution is not too broad. Furthermore, the high molecular weight tail of the thermally polymerized polystyrene samples is difficult to analyze with the accuracy needed for such calculations; in addition to that, it causes experimental difficulties by increasing the viscoelasticity of the solutions (Weissenberg effect). Thus all experiments reported henceforth are carried out with the anionically prepared samples.

To study the scission of chains without the interference of recombination, all experiments described here are performed in the presence of either oxygen or DPPH. In both cases the number of radical scavenger molecules exceeds the number of chains greatly (see above). The degradation experiments are now characterized by the following set of parameters: (1) starting molecular weight, (2) type of added radical scavenger, (3) concentration, and (4) shear rate. The temperature was kept above the temperature of phase separation. Therefore an additional parameter ΔT is given by the distance of the actual temperature from the cloud point temperature of the respective solution. Theoretical considerations[20,21] and measurements of the turbidity of solutions near demixing[22-26] clearly reveal that the homogeneous region is enlarged by stirring. Since the parameter ΔT refers to the cloud point at zero rate of shear, the distance to the actual temperature of phase separation under shearing is larger. From the data in ref 22 the effect can be estimated not to exceed 1–2 K. Thus it is in the range of uncertainty of the determination of temperature in the gap (see above) and will not be considered further here.

Organization of the Presentation. In what is to follow we first discuss the influence of different radical scavengers on the degradation process. Then the results of the fits of the various models introduced in part 1 are presented. After this we discuss the influence of polymer concentration, the influence of the temperature distance to the corresponding demixing temperature (ΔT), and finally the dependence on shear rate.

Influence of Radical Scavenger. As a first outstanding result it can be stated that oxygen and DPPH have a different influence on the degradation process. Figure 3 shows a comparison of the starting molecular weight distribution and the distributions when practically no more scission occurs (after reaching $P_{n,\infty}$). The corresponding plot of the number of broken bonds per molecule B vs. time is given in Figure 4. Figure 5 demonstrates that this difference is even more pronounced at greater distance ΔT to the cloud point temperature. Generally, it can be stated that when DPPH is used, the initial rate of degradation, $(dB/dt)_{t=0}$, is higher than in the presence of oxygen, but in the latter case the resulting B_∞ value is higher; i.e., the limiting molecular weight is lower (cf. eq 8). This is not only true for the polystyrene with P_w = 6.70 × 10^3 but is also found for the high molecular weight sample (P_w = 1.80 × 10^4).

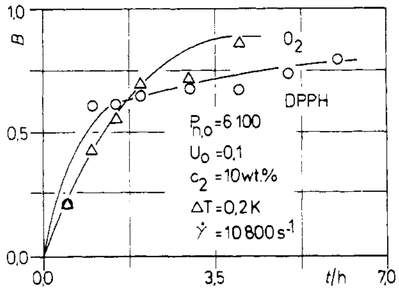

Figure 4. B, the number of broken bonds per chain, (cf. part 1, eq 25), vs. degradation time in the presence of two different radical scavengers. U_0 denotes the molecular nonuniformity ($P_w/P_n - 1$) at t = 0, and ΔT is the distance to the actual demixing temperature.

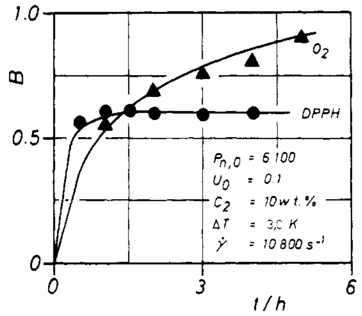

Figure 5. B, the number of broken bonds per chain (cf. part 1, eq 25), vs. degradation time in the presence of two different radical scavengers, U_0 denotes the molecular nonuniformity ($P_w/P_n - 1$) at t = 0, and ΔT is the distance to the actual demixing temperature.

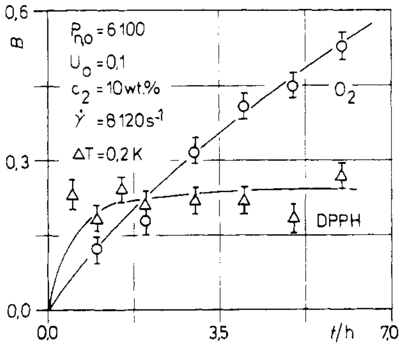

Figure 6. B, the number of broken bonds per chain (cf. part 1, eq 25), vs. degradation time in the presence of two different radical scavengers.

B_∞ for the experiment in the presence of oxygen cannot be obtained directly from the corresponding plot but has to be calculated by the extrapolation procedure mentioned above. It is found to be markedly higher than that resulting from addition of DPPH. Figures 4 and 5 refer to experiments made at $\dot{\gamma} = 10\,800\ \mathrm{s}^{-1}$. At lower shear rate the difference in the shape of the B vs. t curves is even higher as can be seen from Figure 6.

As a simple and self-suggesting explanation for this unexpectedly different behavior of both radical scavengers, one might assume that oxygen as a diradical at first reacts with a C radical. This peroxy radical again reacts with another C radical, yielding a polymer chain of approximately the same length as the starting material. Consequently, this recombination would lead to a smaller rate of degradation. Assuming this model, however, it is not quite obvious how to explain the higher B_∞ values resulting in the presence of O_2. If the weaker peroxy bond is supposed to break again, this clearly should lead to the same result as obtained from experiments using DPPH. As already mentioned the number of oxygen molecules greatly exceeds the number of broken bonds in the system so that a reaction of the fragments with oxygen is more likely than any recombination. The marked influence of the thermodynamic conditions as expressed by ΔT (compare Figures 4 and 5) and of the shear rate (Figure 6) provides further evidence against the above explanation. It is hard to believe that a recombination reaction should be influenced to such an extent just by changing solvent power. At lower shear rate the average concentration of radical fragments in the solution is smaller and the concentration of oxygen is the same, of course. Thus, the probability of recombination is even smaller and the difference in the behavior of oxygen and DPPH should diminish. Figure 6 in comparison to Figure 4 clearly indicates that just the opposite holds true. The most plausible explanation of this behavior is that DPPH as a molecule which contains three phenyl groups is partially adsorbed onto the chain. By this preferential adsorption the solvent quality is improved, and the results in the presence of DPPH are comparable to those obtained with O_2 at higher distance to the demixing conditions. This will be discussed further below.

Comparison with Different Breakage Models. Another interesting point is the result of the fit of different breakage models (random scission, central scission, and Gaussian scission; cf. part 1) to the experimental distributions. Only a Gaussian breakage probability with the center at the midpoint of the chain (cf. part 1, eq 29) was found to reproduce the experimental distributions. This model is characterized by the parameter R, denoting the normalized standard deviation (part 1, eq 26), and the exponent X (eq 28 of part 1), which describes the overall dependence on the individual chain length. Figure 7 shows typical examples for such fits. The agreement is excellent up to $B = 0.8$. At higher values the best fit that can be obtained shows deviations from the experimental distribution. As the maximum number of broken bonds per chain, B_∞, is approached, the deviation becomes even greater. This can be easily explained by the fact that at higher conversion all parameters governing the degradation process, for instance, the viscosity or the distance to the demixing conditions, become markedly different from the starting values. As a consequence mainly of the decrease of the viscosity, the constant k (see above) adjusting the $k_{i,j}$ to the experimental rate of scission decreases slowly with increasing B. The accuracy of the determination of the model parameters R and X can be tested by comparing to the experimental distribution the best fit that is obtained for greater values of X. This is done in Figure 8. Comparing Figure 7a to Figure 8, one can easily see that $X = 0.5$ provides a better fit. By doing such a comparison for more than one experimental distribution, the evaluation

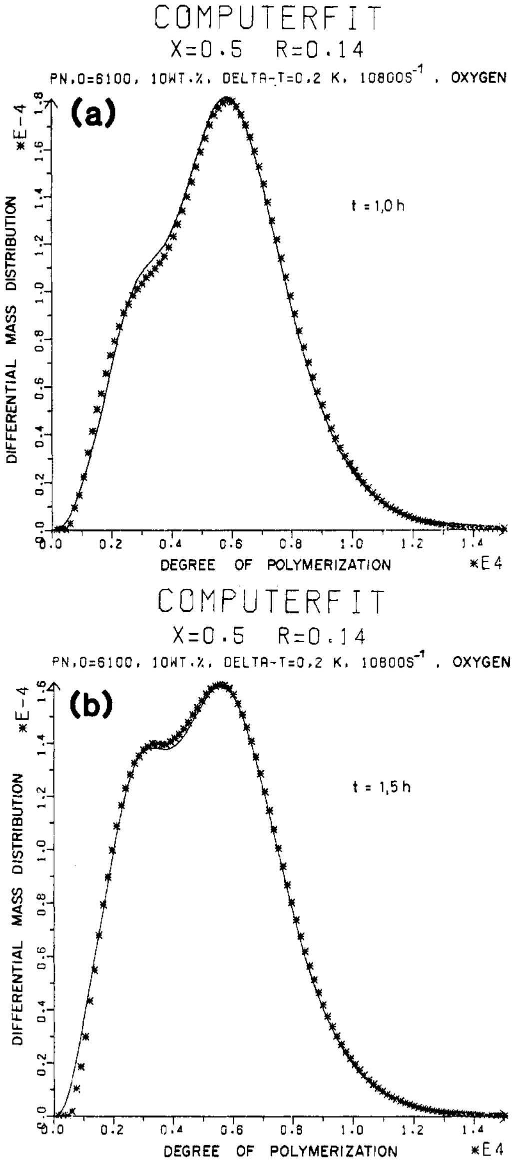

Figure 7. Fit for the model parameters X and R characterizing the Gaussian breakage probability (cf. part 1) to experimental molecular weight distributions.

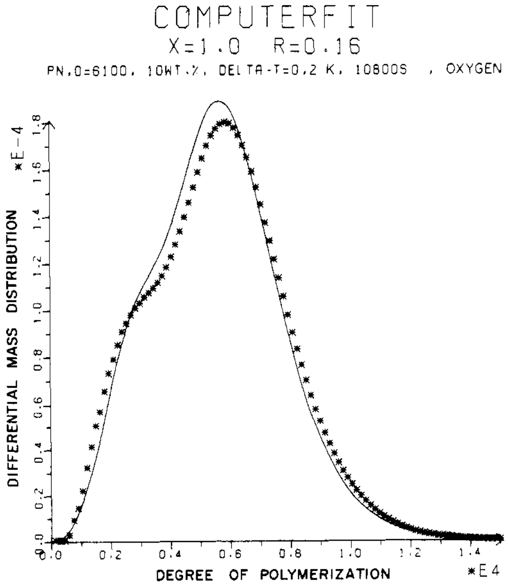

Figure 8. Best obtainable fit for the model parameter R (Gaussian scission; cf. part 1) for a fixed value of the exponent X.

Table I
Influence of Radical Scavengers[a]

$P_w \times 10^{-3}$	ΔT, K	c_2, wt %	$\dot{\gamma}$, s^{-1}	rad sc	$(dB/dt)_{t=0}$, h^{-1}	B_∞	X	R
18	4.5	6.9	10800	O_2	0.41	1.27	0.1	0.16
18	4.5	6.9	10800	DPPH	1.56	0.91	0.2	0.13
18	20.0	6.9	10800	O_2	0.13	0.30	0.3	0.12
18	20.0	6.9	10800	DPPH	0.30	0.18	0.1	0.14
6.70	0.2	10.0	10800	O_2	0.56	0.92	0.5	0.14
6.70	0.2	10.0	10800	DPPH	0.84	0.74	0.5	0.14
6.70	0.2	10.0	8120	O_2	0.12		0.1	0.13
6.70	0.2	10.0	8120	DPPH	0.43	0.22	0.3	0.19
6.70	3.0	10.0	10800	O_2	0.81	0.85	0.7	0.11
6.70	3.0	10.0	10800	DPPH	3.32	0.60	0.7	0.16

[a] ΔT is the distance to the demixing temperature, c_2 is the polymer concentration, $\dot{\gamma}$ is the shear rate, $(dB/dt)_{t=0}$ is the initial rate of degradation (cf. eq 10), B_∞ is the maximum number of broken bonds per molecule (cf. eq 8), and X and R are parameters characterizing the Gaussian breakage probability (cf. part 1).

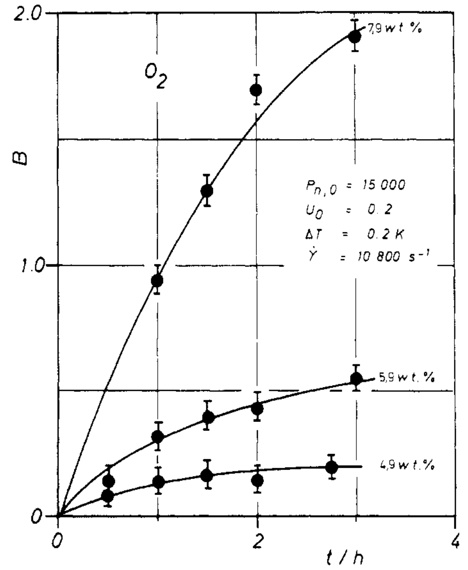

Figure 9. Influence of concentration: B, the number of broken bonds per chain (cf. part 1, eq 25), vs. degradation time for three different polymer concentrations. U_0 denotes the molecular nonuniformity $(P_w/P_n - 1)$ at $t = 0$, and ΔT is the distance to the actual demixing temperature.

of X and R becomes even more secure. Similar arguments show that the uncertainty of R amounts to ±0.03. Table I summarizes all data obtained up to now.

Influence of Concentration. We now turn to the dependence of the degradation process on concentration. All of the following described experiments are obtained with oxygen as a radical scavenger. As discussed above, DPPH has an influence on solvent power whereas the results obtained in presence of oxygen reflect the "unperturbed" scission process. Theoretical considerations due to Bueche[27] predict that only entanglements between different chains are able to cause forces high enough to split the C–C bond. Therefore, an increase of concentration, which leads to higher mutual interactions of the coils, should be followed by a higher rate of degradation. Figure 9 demonstrates that this is, in fact, observed.

Thus the prediction of Bueche's theory is confirmed at least qualitatively. For all experiments shown in Figures 7 and 8 the exponent X amounts to 0.1. So the dependence on actual chain length is not so pronounced. Therefore even shorter chains should be degraded if the concentration is high enough. Thus the polystyrene sample with $P_w = 2.80 \times 10^3$ is degraded when the concentration is 20 wt %. The corresponding $(dB/dt)_{t=0}$ amounts to 0.07 h^{-1} and is still comparatively large (compare Table I.) X and R are given by 0.7 and 0.11, respectively. Thus, even for such short chains, the dependence on the actual molecular weight is quite small, whereas the normalized standard deviation is, within experimental uncertainty, identical with that measured for much higher molecular weights.

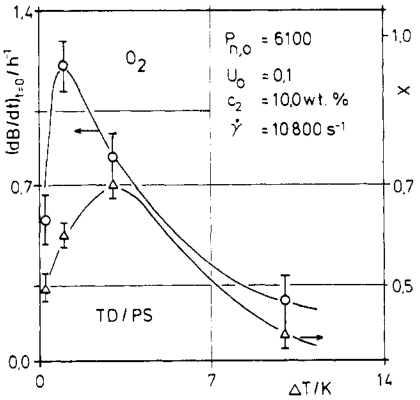

Figure 10. Influence of temperature: initial rate of degradation $(dB/dt)_{t=0}$ (cf. eq 10) and exponent X (Gaussian scission; cf. part 1) vs. ΔT (distance to the actual demixing temperature. U_0 denotes the molecular nonuniformity $(P_w/P_n - 1)$ at $t = 0$.

Influence of Temperature. Since the scission of the C–C bonds occurs only under thermodynamically poor conditions, this effect should become smaller with increasing temperature. As can be seen from Figure 10 this is actually observed, but the dependence on temperature is more complicated than expected from these considerations. In fact, $(dB/dt)_{t=0}$ is much smaller when the temperature is raised to 10 K above the cloud point, but there is a pronounced maximum at $\Delta T = 1$ K. The dependence on chain length as reflected by X exhibits a similar behavior. Except for the variation of X these features are not restricted to $P_w = 6.70 \times 10^3$ but can be also observed when carrying out the experiments with the high molecular weight sample.

The variation of $(dB/dt)_{t=0}$ with increasing distance from the demixing point obtained from experiments in the presence of O_2 now can explain the influence of DPPH on the degradation process. Figure 10 demonstrates that in the region close to demixing ($\Delta T \leq 1$ K), the improving of the solvent quality leads to a higher initial rate of degradation $(dB/dt)_{t=0}$ but lowers the resulting B_∞. The same features are observed on addition of DPPH. Therefore, as already argued above, assuming that DPPH improves the solvent quality provides an explanation for the different effect of both radical scavengers.

The dependence of $(dB/dt)_{t=0}$ and X on temperature furthermore gives a deeper insight into the molecular mechanism of scission. Measurements of the viscosity coefficient of the system toluene/polystyrene and *trans*-decalin/polystyrene[3] have already revealed striking differences between the flow curves of polystyrene in good and in poor solvents. The modified Graessley theory[3] was proved to provide an excellent description of the data for both types of solutions. In this theory the viscosity coefficient is split into an entanglement part η_{ent}, given by Graessley's theory, and an empirical parameter η_{fric} independent of shear. It has been shown[3] that η_{fric} is nearly zero in the good solvent (toluene) so that the pure entanglement term is sufficient to describe the flow curves in this case, but η_{fric} cannot be neglected when the solvent quality is poor. At higher shear rate η_{fric} even may become the leading term. This has been explained by the fact that in a poor solvent the contacts between the polymer segments are energetically favored. This obviously leads to a higher frictional resistance, which is quantitatively measured by η_{fric}. In a shearing field the coil is forced to rotate and has to disentangle from other coils. The hindrance on this disentanglement process effected by the favored contacts between the segments can be so high that the C–C bonds are split. So the present experiments suggest that degradation under laminar conditions only takes place when η_{fric} is not equal to zero. In a good solvent the contacts between the polymer segments and the solvent molecules are favored. Thus the solvent acts as a "lubricant" and lowers the frictional resistance to flow. The shear rate to cause scission under such circumstances is therefore much higher. So the thermodynamically induced shear degradation results from a hindrance on the disentanglement process by frictional forces due to the favored segment–segment contacts. Thus it is reasonable to expect a higher rate of degradation with increasing η_{fric}. Furthermore, a higher η_{ent} clearly reflecting a greater number of entanglements should cause an increase of $(\mathrm{d}B/\mathrm{d}t)_{t=0}$ too. So it is possible to correlate the actual variation of $(\mathrm{d}B/\mathrm{d}t)_{t=0}$ with the dependence of η_{fric} and η_{ent} on temperature and shear rate. At intermediate shear rates the variation of η_{ent} with ΔT just above the demixing point has been shown to be small; going to higher shear rates produces an inversion leading to negative apparent energies of activation for η_{ent}.[3] These peculiarities of the entanglement part have been demonstrated to be consistent with Graessley's theory.[3] Just above the cloud point the dependence of η_{fric} (which is independent of shear) on ΔT is small so that the increase of $(\mathrm{d}B/\mathrm{d}t)_{t=0}$ vs. ΔT is explained by an increase of η_{ent} in the neighborhood of the demixing conditions. The decrease of both η_{fric} and η_{ent} at higher temperatures than leads to a decrease of $(\mathrm{d}B/\mathrm{d}t)_{t=0}$. The maximum of the initial rate of degradation thus can be explained quite naturally. The reason for the unexpected observation that η_{ent} has a negative apparent energy of activation[3] lies in the fact that the entanglement density is lowered when the shear rate becomes higher and higher,[28] meaning a smaller overlap of the coils. In a poor solvent, close to demixing, the actual chain dimensions are smaller than at $T = \Theta$. Raising the temperature is followed by the expansion of the coils, leading to a greater mutual interaction. At constant shear rate the entanglement density therefore becomes higher with increasing ΔT. This change of the coil dimensions, which has been elucidated by recent neutron scattering experiments,[29] not only explains the behavior of η_{ent} above the demixing temperature but also accounts for the maximum of X vs. ΔT. When the interaction between the chains is great because of a high overlap and/or the thermodynamically favored contacts between the segments close to demixing, it is resonable to assume that the individual chain length is of smaller importance. Under such circumstances X is small and becomes greater with increasing temperature because of the weak interactions of the segments. At still higher temperature, the greater mutual interactions of the chains caused by the expansion of the coils again lead to a decrease of X. Since the chain overlap at $T = \Theta$ which is approximately given[30] by $c_2[\eta]$ (c_2 is the concentration of polymer in g/cm^3) amounts in both cases to 4.6, these experiments can be compared to those carried out with the high molecular weight ($P_w = 1.80 \times 10^3$) at a lower concentration (6.9 wt %). Here, in nearly all cases studied so far, X is given by 0.1. Because of the greater length of the chains, the entanglement effects are obviously predominant even at the highest shear rates under consideration.

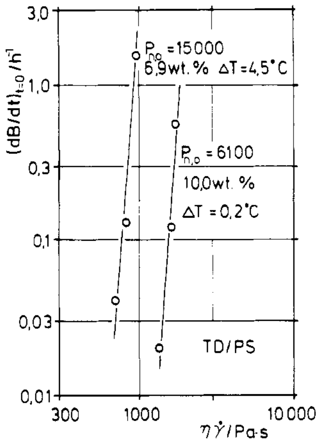

Figure 11. Influence of shear rate: initial rate of degradation $(\mathrm{d}B/\mathrm{d}t)_{t=0}$ (cf. eq 10) vs. shear rate for two different starting molecular weights. ΔT denotes the distance to the actual demixing temperatures.

Influence of Shear Rate. At this point a comparison of experiments obtained at different shear rates can give additional useful information. As already mentioned the viscous heating might lead to a slightly higher temperature in the gap depending on shear rate. For the present purpose of a qualitative comparison this inference, however, should be of minor importance. From most general considerations one expects the rate of degradation to increase with increasing shear rate. Figure 11 shows $(\mathrm{d}B/\mathrm{d}t)_{t=0}$ as a function of $\dot{\gamma}$ in a double-logarithmic plot. It can be seen that in this semiconcentrated regime the influence of the shear rate is very pronounced. Furthermore, the variation of the exponent X with $\dot{\gamma}$ gives deeper insight into the mechanism of degradation. According to Graessley's theory, the entanglement density decreases with increasing shear rate. X should become higher at higher shear rate since the individual molecules can move more independently and reflect their individual parameters. Furthermore, η_{ent} exhibits the negative apparent energy of activation only at very high shear rates; from the above considerations $(\mathrm{d}B/\mathrm{d}t)_{t=0}$ is expected to decrease monotonically with increasing temperature when the shear rate is lower. Table II shows that both predictions are confirmed by the experiments. Furthermore, it can be seen that at lower $\dot{\gamma}$ and/or higher ΔT, R becomes very small; i.e., the chains are practically split at the midpoint only.

These results clearly demonstrate that the variation of the parameters characterizing the degradation can be predicted, at least in a semiquantitative manner, in terms of the modified Graessley theory. Thus, the underlying model seems to be an adequate description of the chain dynamics in a shearing field. Bueche's theory, which clearly recognizes the importance of entanglements,[27] fails

Table II
Influence of the Shear Rate[a]

ΔT, K	$\dot{\gamma}$, s^{-1}	$(\mathrm{d}B/\mathrm{d}t)_{t=0}$, h^{-1}	X	R
0.2	5400	0.02	0.1	0.03
0.2	8120	0.12	0.1	0.13
0.2	10800	0.56	0.5	0.14
3.0	8120	0.03	0.1	0.03
3.0	10800	0.81	0.7	0.11

[a] $P_w = 6.70 \times 10^3$ ($t = 0$), concentration = 10.0 wt %, radical scavenger = O_2. ΔT is the distance to the demixing temperature, $\dot{\gamma}$ is the shear rate, $(\mathrm{d}B/\mathrm{d}t)_{t=0}$ is the initial rate of degradation (cf. eq 10), and X and R are parameters characterizing the Gaussian breakage probability (cf. part 1).

to predict resonable values for X and R. According to this model, X should be 2 and the breakage probability is predicted to be sharply peaked at the center of the chain. In contrast to this, X is usually found to be much lower when the experiments are carried out in the semiconcentrated region (cf. ref 31). The chains are only split practically at the midpoint when the shear rate is very small or the distance to demixing is high.

Conclusion

It has been shown that the degradation of polystyrene at moderate shear rates in *trans*-decalin is induced by the poor solvent quality. This demonstrates that the dynamics of the chain in this concentration regime is strongly influenced by the thermodynamic conditions. The present results furthermore suggest that the model given by the modified Graessley theory provides a good description for the motion of the chains in a sheared liquid. Thus, degradation experiments are a useful tool for studying the chain dynamics in semiconcentrated polymer solutions. Furthermore, they can give a deeper insight into the mechanism of drag reduction.[32]

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

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