Peterlin theory leads to an extra adjustable parameter, the actual physical meaning of which is poorly understood.

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Relationship between Hydrodynamic Volume and the Scission of Polymer Chains by High-Speed Stirring in Several Solvents

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ABSTRACT: Five different vinyl polymers, poly(methyl methacrylate), poly(methyl acrylate), poly(α-methylstyrene), polystyrene, and polyisobutylene, were stirred at 30,000 rpm by a T. K. Homomixer at a polymer concentration of 0.04% w/v in various solvents for 2 hr in order to investigate the relationship between final chain length and the hydrodynamic volume of the polymer chains in the solvents. After prolonged stirring at low concentration the ruptured polymer chains reached a nearly constant hydrodynamic volume independent of the type of solvent, and polymers with higher T_g's, i.e., the more rigid polymers, attained lower hydrodynamic volumes. The results indicate that there is a relation between mechanical scission of polymer chains in solution and their hydrodynamic volume.

The authors have been studying various factors which affect the scission by high-speed stirring[1–5] of solutions of long-chain polymers such as poly(methyl methacrylate) and polystyrene. It has been found that the rate of scission of polymer chains is higher and the final chain length is shorter in good than in poor solvents at a low concentration.[4] Because polymer chains are more extended and thus have larger intrinsic viscosities in good than in poor solvents, the products of final chain lengths and their intrinsic viscosities in the results[4] seemed to approach a constant value regardless of the kinds of solvents used at low concentrations. According to Flory,[6] the following equation holds for polymers in solution

$$[\eta]M = \Phi(6\bar{S}^2)^{3/2}$$

where $[\eta]$ is the intrinsic viscosity, M is the molecular weight, Φ is the Flory constant, and $(\bar{S}^2)$ is the mean-square distance of an element from the center of gravity. Therefore, the products described above can be estimated in terms of hydrodynamic volumes.

In this study, the relationship between hydrodynamic volumes and the final chain lengths of various polymers was investigated after stirring at low concentration in several solvents.

Experimental Section

Materials. The linear long-chain polymers used for degradation were prepared as follows. Poly(methyl methacrylate) (PMMA) was prepared in the same way as described in a previous paper.[4] Viscosity average degree of polymerization, ($\bar{P}_v$), was 6250 and molecular weight, ($\bar{M}_v$), was 625,000. Polystyrenes (PSt-1 and PSt-2) with different molecular weights and molecular weight distributions were used. PSt-1 was described in the previous paper[4] and PSt-2 was obtained from Pressure Chemical Co. $\bar{P}_v$ of PSt-1 was 5610 and $\bar{M}_v$ was 583,000. The nominal molecular weight and $\bar{M}_w/\bar{M}_n$ of PSt-2 were 2,000,000 and less than 1.30, respectively. $\bar{P}_v$ and $\bar{M}_v$ of PSt-2 measured by the authors were 15,300 and 1,590,000, respectively. Poly(methyl acrylate) (PMA) was spontaneously polymerized by sunlight in a sealed glass container in the absence of initiator. $\bar{P}_v$ was 17,800 and $\bar{M}_v$ was 1,530,000. Poly(α-methylstyrene) (PαMSt) was obtained by polymerizing the purified monomer using living tetramer of α-methylstyrene obtained by reacting the monomer with sodium metal in THF. $\bar{P}_v$ was 8980 and $\bar{M}_v$ was 1,060,000. Polyisobutylene (PIB) (Vistanex MML-100 supplied by Esso Standard Petroleum Co.) had a $\bar{P}_v$ of 16,500 and a $\bar{M}_v$ of 927,000. Solvents were used after purifying by the usual methods. The $\bar{P}_v$ and $\bar{M}_v$ values listed for the above polymers were determined from equations contained in the next section.

Procedure. Solutions of each polymer (200 ml) in each solvent at a given concentration were prepared and stirred at 30,000 ± 500 rpm at 30 ± 5° for a given time by a high-speed mixer. The experiments with PSt–cyclohexane were carried out at 40 ± 5°. The

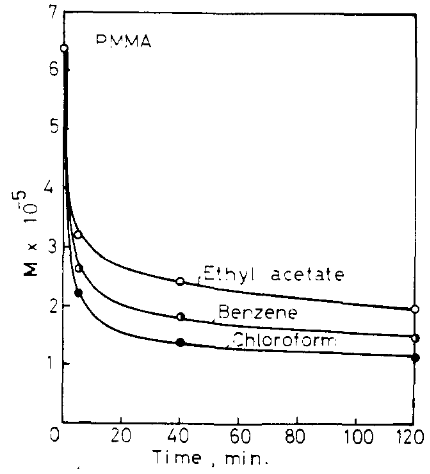

Figure 1. Falloff in molecular weight of PMMA in various solvents at 0.04% w/v during high-speed stirring (30,000 rpm, 30°, 0.04% w/v): (○) ethyl acetate; (◑) benzene; (●) chloroform.

stirred polymer was recovered by evaporating the solvent and intrinsic viscosities were measured at 30 ± 0.02° in benzene, $[\eta]_B$, and in each solvent used for stirring, $[\eta]_S$. However, the intrinsic viscosity of PSt–cyclohexane was measured at 40° with an Ubbelohde viscometer.

Chain lengths of polymers $\bar{M}_v$ or $\bar{P}_v$ were calculated from the following equations.

PMMA[7] $\bar{P}_v = 2200[\eta]_B{}^{1.13}$

PMA[8] $[\eta]_B = 4.5 \times 10^{-5}\bar{M}_v{}^{0.78}$

PαMSt[9] $[\eta]_B = 24.9 \times 10^{-5}\bar{M}_v{}^{0.647}$

PSt[10] $\bar{P}_v = 1770[\eta]_B{}^{1.40}$

PIB[11] $[\eta]_B = 6.1 \times 10^{-4}\bar{M}_v{}^{0.56}$

It is more accurate to use the number average degree of polymerization, $\bar{P}_n$, to calculate the number of scissions described below, since the molecular weight distribution varies with the scission of polymer chains. However, either $\bar{P}_v$ or $\bar{M}_v$ was used here for convenience. Gel permeation chromatographs for PMMA before stirring and after 2 hr of stirring gave nearly Gaussian distributions,[5] which are not shown here. The above equations, therefore, were assumed to be valid for polymers in this study.

Stirring apparatus and procedure were described in detail in the previous paper.[1] A T. K. Homomixer of the M type made by Tokushu Kika Kogyo was used as a high-speed stirrer.

Results and Discussion

Scission of PMMA in Various Solvents by High-Speed Stirring. The scission of PMMA chains in various solvents by high-speed stirring is shown below. The solutions containing PMMA in chloroform, benzene, and ethyl acetate at 0.04% w/v were prepared and stirred for given times at 30,000 rpm at 30°. Molecular weights of polymers recovered after stirring are shown in Figure 1. They decreased rapidly at first and then more slowly. The polymers were still degrading even after 2 hr of stirring. However, molecular weights obtained by stirring for 2 hr seem to approximate rather closely the final chain lengths for each solvent. Molecular weights of PMMA stirred at 0.04% w/v for 2 hr were highest for the poorest solvent, ethyl acetate; medium for the medium solvent, benzene; and lowest for the good solvent, chloroform.

Table I
Values of k and P_1 for PMMA Solutions of Various Concentrations (30,000 rpm, 30°)

Solvent	Concn, % w/v	$k \times 10^6$, min^{-1}	P_1	$P_\infty = {}^3\!/\!_4 P_1$	$\bar{P}_{2\,\mathrm{hr}}$
Ethyl acetate	2	13	3500	2630	2770
	0.2	14	3170	2380	2490
	0.04	21	2580	1940	1970
Benzene	2	14	4440	3330	3400
	0.2	22	3060	2300	2300
	0.04	30	1920	1440	1470
Chloroform	2	10	4560	3420	3600
	0.2	20	2110	1580	1650
	0.04	40	1510	1130	1150

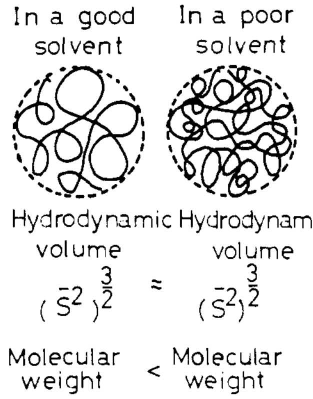

Figure 2. Models of polymer in solvents after prolonged stirring.

The $\bar{M}_v$ vs. time curves can be converted to scission number vs. time plots by the method described in the previous paper[1] and expressed by Ovenall's equation $dB_i/dt = kn_i(P_i - P_1)$, where k is the rate constant of scission and P_1 the limiting degree of polymerization below which polymers cannot be ruptured. Values of k and P_1 calculated by the method described in the previous paper[1] for experimental results on PMMA solution at various concentrations are shown in Table I. $\bar{P}_\infty$ and $\bar{P}_{2\mathrm{hr}}$ in Table I represent the degrees of polymerization after infinite and 2-hr stirring, respectively.

It is clear that P_1 is higher at higher concentration in every solvent and that at the lowest concentration, 0.04% w/v, P_1 is higher in the poor solvent, and is lower in the good one. The latter observation seems to suggest that polymer chains degrade to a nearly constant hydrodynamic volume in those solvents. Because the interaction between polymer molecules is smaller and the rate of scission is higher at low concentrations, it seemed to be more appropriate to investigate the effect of solvent on the scission of polymer chain or to study the relationship between the final chain length and the hydrodynamic volume at lower concentration. At the lowest concentration, the values of $\bar{P}_{2\mathrm{hr}}$ are very close to those of $\bar{P}_\infty$, indicating that they represent to a considerable extent the final values obtained from infinite stirring.

Relationship between Final Chain Length and Hydrodynamic Volume. As seen above, $\bar{P}_{2\mathrm{hr}}$, the degree of polymerization after 2 hr of stirring of a 0.04% solution was regarded as the value of final chain length. $\bar{P}_{2\mathrm{hr}}$ obtained for various polymers in several solvents are shown in Table II with other related values.

The values of $\bar{M}_{2\mathrm{hr}} \times [\eta]_S$ were nearly constant regardless of the kind of solvent used for each polymer except the PαMSt–benzene, PSt–toluene, and PSt–benzene systems. $\bar{M}_{2\mathrm{hr}} \times [\eta]_S$ are values proportional to the hydrodynamic volumes. Therefore the calculated results mean that polymer chains were degraded to a nearly constant hydrodynamic volume in every solvent by high-speed stirring after relatively long time intervals as shown by models in Figure 2. Viewed from the standpoint of chain length, the values of P_1 were scattered but if they are observed from the

Table II
Degree of Polymerization, Intrinsic Viscosity, and Values Relating to Hydrodynamic Volume for Polymers Stirred for 2 hr in Various Solvents at 0.04% w/v by High-Speed Stirring (30,000 rpm, 30°)[a]

Polymer	Solvent	$\bar{P}_{2\text{hr}}$	$[\eta]_S$, dl/g	$\bar{P}_{2\text{hr}}[\eta]_S$, dl/g	$\bar{M}_{2\text{hr}}[\eta]_S = (6\bar{S}^2)^{3/2}\Phi$, 10^5 dl/g
PMMA	Chloroform	1150	0.873	1000	1.00
$\bar{P}_0$ = 6250	Benzene	1470	0.700	1030	1.03
T_g = 105°	Ethyl acetate	1970	0.540	1060	1.06
PMA	Chloroform	2830	1.125	3180	2.83
$\bar{P}_0$ = 17,800	Benzene	3970	0.937	3720	3.32
T_g = 6°	Ethyl acetate	3930	0.830	3260	2.81
PαMSt	Benzene	2020	0.750	1515	1.79
$\bar{P}_0$ = 8980	Dioxane	1250	0.540	680	0.80
T_g = 170–192°	Chloroform	1390	0.520	720	0.85
PSt	Benzene	1910	1.057	2020	2.10
$\bar{P}_0$ = 5610	Toluene	2080	1.040	2160	2.25
T_g = 100°	Dioxane	1340	0.770	1030	1.07
	Chloroform	1060	0.830	880	0.91
	Ethyl acetate	2000	0.500	1000	1.04
	Methyl ethyl ketone (MEK)	2230	0.555	1240	1.29
PSt	Benzene	2330	1.218	2840	2.95
$\bar{P}_0$ = 15,300	Toluene	2260	1.095	2470	2.57
	Dioxane	1460	0.783	1140	1.19
	Chloroform	1030	0.731	753	0.78
	Ethyl acetate	1810	0.503	910	0.95
T_g = 100°	MEK	1870	0.560	1050	1.09
	Cyclohexane[b]	2210	0.502	1110	1.15
	1,2-Dichloroethane	1530	0.723	1110	1.15
PIB					
$\bar{P}_0$ = 16,500	*n*-Hexane	1800	0.720	1260	0.71
T_g = −73°	Benzene	3270	0.530	1730	0.97

[a] $\bar{P}_0$ and $\bar{P}_{2\text{hr}}$ are the $\bar{P}_v$ of polymers before stirring and after 2 hr of stirring at 0.04% w/v, respectively. $[\eta]_S$ is the $[\eta]$ of the polymer in the solvent after stirring for 2 hr. [b] Data at 40°.

standpoint of hydrodynamic volume, they converge to a nearly constant value or final hydrodynamic volume independent of the type of solvent.

The results obtained for two types of PSt with different molecular weights and molecular weight distributions (MWD) are shown in Table II. The values for the same solvent were not identical but were scattered. However, no meaningful difference was found between the two kinds of PSt. It was found that PSt chains were ruptured to a nearly constant hydrodynamic volume regardless of MWD of initial polymer and solvent.

The Mark–Houwink–Sakurada equations used to obtain $\bar{P}_v$ or $\bar{M}_v$ are varied and Flory's constant, Φ, can vary with the type of polymer. Therefore it would be a mistake to regard the values of $\bar{M}_{2\text{hr}}[\eta]_S$ as being precisely proportional to $(\bar{S}^2)^{3/2}$ and to use them for comparisons between different polymers even if it is possible for a single polymer. Nevertheless, comparisons were made between polymer analogs.

It is found that the values of $\bar{M}_{2\text{hr}}[\eta]_S$ for PMMA and PαMSt are smaller than those for PMA and PSt and that the former polymers gave a smaller hydrodynamic volume than the latter. PMMA and PαMSt are considered to be derivatives of PMA and PSt whose hydrogen atom on *α* carbon is substituted with a methyl group and as a result the rotation of the main chains of the methyl substituted polymers are more restricted than those of PMA and PSt. Rigidities of PMMA and PαMSt are thought to be higher than those of PMA and PSt and, as shown in Table II, the glass transition temperature, T_g, increases with chain stiffness. Consequently, the experimental results show that chain scission by a shearing force depends on the rigidity of a polymer chain and that a main chain with higher rigidity is more easily broken. There might be some relation between dimensions of the hydrodynamic volume and the rigidities of polymers.

The values of $\bar{M}_{2\text{hr}}[\eta]_S$ for PIB were rather small. Unfortunately, no corresponding derivative polymer, i.e., polypropylene, with a high enough $\bar{M}_v$ for degradation could be obtained for comparison.

The above data on $\bar{M}_{2\text{hr}}[\eta]_S$ were widely scattered for PSt and PαMSt in benzene and toluene, showing that their molecular volumes after breaking were about twice as large as those of the other polymers. The reason for the scattering is unknown. It may be possible that the rate of degradation for these systems was too low for $\bar{M}_{2\text{hr}}$ to represent the final chain length. Furthermore it might be caused by other factors relating to bond scission in the macromolecules. If experiments had been carried out at lower concentrations, the data on $\bar{M}_{2\text{hr}}[\eta]_S$ may have shown less scattering.

Mechanism of Scission. The results can be interpreted as follows. Polymer molecules were so well extended in good solvents that the larger molecules received a strong enough shear stress to break main chains into shorter segments. Under identical experimental conditions, molecules ruptured to below a certain limiting hydrodynamic volume no longer are subject to shear forces large enough to cause further chain scission.

If polymer chains are ruptured to a constant hydrodynamic volume, it is reasonable to assume that they are broken to a shorter average chain length in a good solvent.

They may be highly extended[12] when they receive a shear stress strong enough to break polymer bonds. According to Harrington and Zimm,[12] polymers are considerably extended under a large velocity gradient and under such conditions the Gaussian coil model is no longer possible. On the other hand, the rate constant of scission is considered to be highest near the center of polymer molecules[13-15] under the conditions described in this report, and it is assumed that the shearing forces become smaller away from the center. Such a heterogeneous distribution of shearing forces along polymer chains might affect the shape of the coils. The authors suppose that polymer molecules are deformed to something like the shape of the infinity symbol, "∞", under such shearing forces. Therefore the models shown in Figure 2 ought to be corrected to flat ellipses or stretched shapes under a high velocity gradient. In any event, the authors suspect from the results that, even under a large velocity gradient, the hydrodynamic volume has a certain relation to the scission of a polymer chain in solution by high-speed stirring.

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Diffusion of Polymers Along a Fluid–Fluid Interface

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ABSTRACT: We evaluate the diffusion coefficient for the motion of a polymer along the interface between two fluids. Two polymer models are considered: rigid rods oriented at right angles to the interface, and spherical molecules with their center in the interface.

I. Introduction

The influence of bounding surfaces on the motion of a solid body immersed in a fluid was first investigated by Lorentz[2a] in 1896. He studied the motion of a sphere near a plane wall using a perturbation method, the so-called method of reflections. Subsequently the effect of wall geometry on the motion of more complicated objects has been studied in great detail by the same method.[2b]

In the present article we consider the effect of geometry on the motion of polymers, regarded as diffuse objects rather than as solid bodies. In particular we study the translational diffusion of a polymer adsorbed at the interface between two immiscible fluids. Our primary motivation for studying this problem is the present interest in interfacial phenomena, particularly with regard to the adsorption and mobility of polymeric species at fluid surfaces. The dynamical behavior of macromolecules along interfaces and near walls is of biological interest and potentially may be studied by light scattering and fluorescence spectroscopy. In addition this problem is of theoretical interest because of the present day concern with two-dimensional transport phenomena and the difficulties encountered in the kinetic theory for the transport coefficients. We consider two polymer models, namely, rigid rods oriented perpendicularly to the interface, and diffuse spheres. In a following article we shall investigate the effect of solid walls on the translational diffusion of rigid rod molecules.

We use an approximate expression for the diffusion tensor in terms of the hydrodynamic interaction tensor and the polymer segment distribution, which is a generalization of an expression derived by Kirkwood[3] for diffusion in bulk fluids. The derivation for limited geometry and a discussion of the approximations involved is given in a separate article.

In section II we consider a planar interface between two immiscible fluids and derive the corresponding fundamental solution of the linear Navier–Stokes equations for steady flow. We assume that the surface tension of the interface is so large that it remains planar. In section III we evaluate the translational diffusion coefficient for a rigid rod molecule oriented perpendicularly to the interface. In section IV we consider a spherical polymer and calculate its diffusion coefficient for motion along the interface. Finally, in section V we show that our assumption of large surface tension is an adequate approximation for the situations of interest.

II. Hydrodynamic Interaction Tensor

We consider a polymer immersed in a fluid described by the creeping motion equations, i.e., the Navier–Stokes