(30) Abe, Y.; Flory, P. J. *Macromolecules* **1971**, *4*, 219, 230.
(31) Ansovena, F. J.; Reveulata, L. M.; Guzman, G. M.; Iruin, J. J. *Eur. Polym. J.* **1982**, *18*, 19.
(32) Mark, J. E. *J. Chem. Phys.* **1972**, *57*, 2541.
(33) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.
(34) Flory, P. J.; Mark, J. E.; Abe, A. *J. Am. Chem. Soc.* **1966**, *88*, 639.
(35) This value is based on data from ref 2, Table I, p 40, obtained at a measurement temperature of ca. 140 °C and corrected by using the temperature coefficient -1.1×10^{-3} (C°)$^{-1}$ of Table II of ref 2.
(36) Stacy, C. J.; Arnett, R. L. *J. Phys. Chem.* **1973**, *77*, 78.
(37) Stacy, C. J.; Arnett, R. L. *J. Phys. Chem.* **1973**, *77*, 1986.
(38) Reference 2, Table I, p 40.
(39) Yamakawa, H. *J. Chem. Phys.* **1961**, *34*, 1360.
(40) Muthukumar, M.; Freed, K. F. *Macromolecules* **1977**, *10*, 899.
(41) Berry, G. C. *J. Chem. Phys.* **1967**, *46*, 1338.
(42) Abdel-Azim, A.-A. A.; Huglin, M. B. *Polymer* **1983**, *44*, 1429.
(43) Peterson, J. M.; Fixman, M. *J. Chem. Phys.* **1963**, *39*, 2516.
(44) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1975**, *62*, 4032.
(45) Imai, S. *Proc. R. Soc. London, Ser. A* **1969**, *308*, 497.
(46) Ogasa, T.; Imai, S. *J. Chem. Phys.* **1971**, *54*, 2989.
(47) Muthukumar, M. *J. Chem. Phys.* **1983**, *79*, 4048.
(48) Gomez, P. A. G.; Barrales-Rienda, J. M.; Aenlle, E. O. *An. Quim.* **1980**, *76*, 357.
(49) Orofino, T. A.; Mickey, J. W., Jr.; *J. Chem. Phys.* **1963**, *38*, 2512.
(50) Orofino, T. A. *J. Chem. Phys.* **1966**, *45*, 4310.
Mays, J.; Fetters, L. J.; Hadjichristidis, N., manuscript in preparation.
(51) Mays, J.; Fetters, L. J.; Hadjichristidis, N., manuscript in preparation.

Dipole Moments of Poly(*N*-vinylcarbazole)

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ABSTRACT: A sample of poly(*N*-vinylcarbazole) (PVK) was synthesized by radical polymerization in toluene solution using azobis(isobutyronitrile) (AZBN) as initiator. The weight-average molecular weight of the polymer, estimated by light scattering measurements in THF solutions, was 4.36×10^5 and its isotactic fraction, determined by ^{13}C NMR, was $P_i = 0.33$. Dipole moments of PVK in dioxane solutions were measured at several temperatures from 30 to 60 °C. The experimental value at 30 °C of the dipole moment ratio $D_x = \langle\mu^2\rangle/x\mu_0^2$ (where $\langle\mu^2\rangle$ represents the mean-square dipole moment of the chains and $x\mu_0^2$ is the same quantity in the idealization that all the skeletal bonds are freely jointed) was found to be 0.43, in very good agreement with the results reported by other authors. The temperature coefficient $\delta \ln \langle\mu^2\rangle/\delta T$, measured in the vicinity of 30 °C was 2.1×10^{-3}. The rotational isomeric states model, with the 2 × 2 states scheme previously employed to study unperturbed dimensions of PVK, was used here to analyze the dipole moment of this polymer. Calculated values of D_x are in reasonable agreement with the experimental results; however, a negative temperature coefficient is predicted by theory.

Introduction

The discovery of electronic transport in vinyl aromatic polymers has emphasized the need for a better knowledge of the structural characteristics of these materials in order to correlate the nature of the electronic properties and its charge generation. One of the polymers which has focused the attention in many aspects for its dielectric, charge-transfer, or energy-transfer properties is poly(*N*-vinylcarbazole) (PVK). Owing to the photoconductivity of these chains which confers practical uses to the polymer, a few studies have been made on the crystalline structure, electric properties, and microstructure by NMR spectroscopy.[1]

Sundararajan[2] carried out the conformational analysis of PVK in terms of pairwise rotations around the skeletal bonds. As occurs with other vinyl chains bearing bulky planar substituents, the side group imposes severe restrictions on the available conformations so that a 2 × 2 rotational isomeric states (RIS) scheme is suitable for the study of the configurational properties of PVK. By using this approach, the rather large unperturbed dimensions of the polymer were successfully explained. It would be desirable to extend this analysis to the study of the polarity of the chains. The aim of this work was, therefore, to measure the dipole moments of PVK chains and to interpret critically the results, using Sundararajan's statistics.

Experimental Section

***N*-Vinylcarbazole (VK).** *N*-Vinylcarbazole monomer (Fluka, A.G.) was recrystallized from methanol three times before use. It was obtained as a pure crystalline white solid with a melting point of 65.5 °C (by DSC at 10 °C/min).

Poly(*N*-vinylcarbazole) (PVK). PVK was synthesized by radical polymerization of *N*-vinylcarbazole in 30% (w/v) toluene solution containing 0.3% azobis(isobutyronitrile) (AZBN). More detailed information is given elsewhere.[3] The polymer was white and powdered, soluble in the usual organic solvents. The intrinsic viscosity at 25 °C, estimated in THF solution, was 32.5 mL/g. The weight-average molecular weight, M_w, estimated by light scattering measurements in THF at 25 °C was 4.36×10^5.

Microstructure of PVK. The steric microstructure of the PVK sample was determined by following the procedure of Kawamura et al.[4] which has been employed very recently by Terrel and Evers[5] to analyze systematically the free radical polymerization of *N*-vinylcarbazole as a function of solvent power and polymerization temperature. ^{13}C NMR spectra were recorded with a Varian XL-100-12FT spectrometer. The measurements were carried out at 90 °C on undegassed 10-mm-o.d. Pyrex NMR glass tube, using 1,4-dioxane-d_8 as ^{2}H internal lock solvent. Other experimental conditions are similar to those reported by Terrel and Evers.[5] The fraction of isotactic dyads P_i was calculated from the areas of the triad peaks (*rr*, 51.3 ppm; *mr*, 50.0 ppm; *mm*, 49.5 ppm) using the expression $P_i = mm + (mr/2)$, where *mm*, *mr*, and *rr* represent the respective triad mole fractions. It was found that $P_i = 0.33$, in satisfactory agreement with the tacticity reported for other PVKs obtained by free radical polymerization at the same temperature.[5]

Dielectric Measurements. Dielectric constants ϵ of solutions of PVK in dioxane were measured with a capacitance bridge (General Radio, Type 1620 A) and a three-terminal cell.[6] The measurements were performed for several frequencies lying in the range 200–20 000 Hz, and no significant dependence of ϵ on frequency was found. Increments in refractive index of the so-

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Table I
Dielectric Constant $d(\epsilon - \epsilon_1)/dw$, Refraction Index $d\Delta n/dw$, Specific Volume dv/dw, and Dipole Moment Ratio $\langle\mu^2\rangle/x\mu_0^2$ Results of Poly(N-vinylcarbazole) (PVK) in Dioxane Solution at Several Temperatures

temp, °C	$d(\epsilon - \epsilon_1)/dw$ at 10 kHz	$d\Delta n/dw$	dv/dw	$\langle\mu^2\rangle/x\mu_0^2$ at 10 kHz
25		0.2475	0.1586	
30	2.99	0.2471	0.1721	0.414
40	2.92	0.2465	0.1702	0.423
50	2.85	0.2460	0.1963	0.431
60	2.79	0.2450	0.2000	0.442

lutions with respect to the solvent were measured with a He–Ne KMX-16 laser differential refractometer (Chromatix, Inc., U.S.A.) operating at 632.8 nm. Specific volumes of the solutions, as a function of the weight fraction of the polymer, were measured by pycnometry over the range 25–60 °C.

Results and Discussion

Dielectric Results. Values of the concentration dependence of the quantities of interest at 30, 40, 50, and 60 °C were expressed as $d\Delta\epsilon/dw$ and $d\Delta n/dw$, where w is the weight fraction of solute in the solution, $\Delta\epsilon = \epsilon - \epsilon_1$ is the dielectric constant of the solution relative to that of the solvent, and Δn serves the same purpose for the index of refraction. The results for solutions of PVK in dioxane are given in Table I. Mean-square dipole moments were calculated by means of the equation of Guggenheim and Smith[7]

$$\langle\mu^2\rangle = \frac{27KTM}{4\pi\rho N_A}\left[\frac{d\Delta\epsilon/dw}{(\epsilon_1 + 2)^2} - \frac{2n_1(d\Delta n/dw)}{(n_1^2 + 2)^2}\right] \qquad (1)$$

where n_1 is the refractive index of the solvent, T is the absolute temperature, k is the Boltzmann constant, N_A is Avogadro's number, M is the molecular weight of the solute, and ρ is the density of the solvent.

Values of the dipole moment ratio $D_x = \langle\mu^2\rangle/x\mu_0^2$, where x is the degree of polymerization and μ_0 is the dipole moment of the repeating unit, are shown in the last column of Table I. The value of μ_0 was assumed to be that of N-isopropylcarbazole,[8] which is 2.93 D. The value of D_x for PVK (0.41 at 30 °C), determined in dioxane, agrees satisfactorily with that reported by North and Phillips,[8] who studied the dielectric behavior of a series of PVK fractions. It should be pointed out that the polarity of PVK, as expressed by the dipole moment ratio, is somewhat lower than that of other vinyl polymers with halogenated side groups such as poly(p-chlorostyrene),[9] in which the value of D_∞, choosing μ_0 = 1.90 D, is 0.688. Finally, the dipole moment ratio corresponding to PVK seems to have a positive temperature dependence.

Theoretical Calculations

(a) Energetic and Geometrical Parameters. In the theoretical analysis of the dipole moments of PVK chains we use the conformational statistics reported by Sundararajan[2] for this polymer. This author used a two-states RIS scheme similar to the one used for some other vinyl polymers bearing a huge and planar substituent (i.e., polystyrene (PS), poly(p-chlorostyrene) (PCS), poly(p-bromostyrene) (PBS), etc.); the statistical weight matrices have been reported elsewhere[2,10,11] and the statistical weights written as a product of a preexponential factor times a Boltzmann constant (i.e., $\xi = \xi_0 \exp(-E_\xi/RT)$) are summarized in Table II. The preexponential factors were computed through calculations of conformational energies of meso and racemic dyads of PVK; the energies shown in Table II were optimized by analysis of some conformational properties.[2]

Table II
Statistical Weights of PVK[a] Written As $\xi = \xi_0 \exp(-E_\xi/RT)$

ξ	ξ_0	E_ξ, kcal/mol
η	1.1	−0.5
ω	1.0	1.9
ω'	0.8	0.5
ω''	0.5	1.0

[a] Taken from ref 2.

Table III
Geometrical Parameters of PVK[a]

state	$\langle\phi_{i-1}\rangle$	$\langle\phi_i\rangle$	θ'	θ''
meso				
tt	20	20	117	112
tg[b]	0	110	114	112
gg	100	100	114	112
racemic				
tt	10	10	117	112
tg[b]	15	100	114	112
gg	110	110	114	112

[a] Taken from ref 2. [b] Includes gt with $\langle\phi_{i-1}\rangle$ and $\langle\phi_i\rangle$ interchanged.

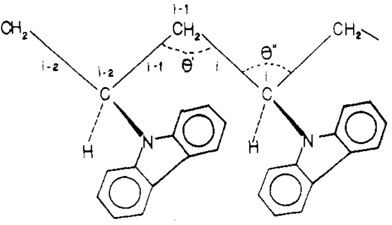

Figure 1. Segment of a meso PVK chain shown in its planar all-trans conformation.

Table III summarizes the geometrical parameters; i.e., torsional and valence angles (see Figure 1) were obtained by averaging ϕ_{i-1} and ϕ_1 in the vicinities of each state with increments of 5°. By symmetry, the dipole moment of the repeating unit should lie along the C^α–N bond. The components of this vector referred to the coordinate system affixed to skeletal bonds $i - 1$ (i.e., C^α–CH_2 bond) are $-0.3207\mu_0$, $0.4755\mu_0$, and $-0.8191\mu_0$, with μ_0 representing the module of the dipole moment of the repeating unit.

(b) Calculation of the Dipole Ratios. The computation scheme reported elsewhere,[2,10,11] which allows the utilization of average location for each state of the bond pair of the dyad, was used to compute $\langle\mu^2\rangle$ of chains consisting of x = 200 repeating units with Bernoullian placement of meso and racemic dyads. The dipole moment ratio reaches its asymptotic limit at $x \simeq 150$ (typical differences between D_{150} and D_{200} are of the order of 0.2%).

Figure 2 shows the value of D_{200} calculated at T = 300 K as a function of the fraction of meso dyads P_i. Values shown for $0 < P_i < 1$ are averages over 10 chains generated as explained above; standard errors of these averages are represented by vertical bars. The variation of D_{200} with the energetic parameters and the temperature is summarized in Table IV.

(c) Discussion. The conformational statistics of PVK,[2] used in the present work, is quite similar to that used by Flory and co-workers[10–13] for PS, PCS, and PBS. A comparison between the statistics of both series of polymers is presented in Table V that summarizes the value of the statistical weights (i.e., the elements of the U″ matrices) and the probabilities of occurrence[14] of each conformation of the bond pair $i,i - 1$ within an infinitely long chain. The influence of the conformation aspects of PVK chain on the unperturbed dimension was already analyzed by Sundararajan;[2] therefore, we shall refer only to the influence of

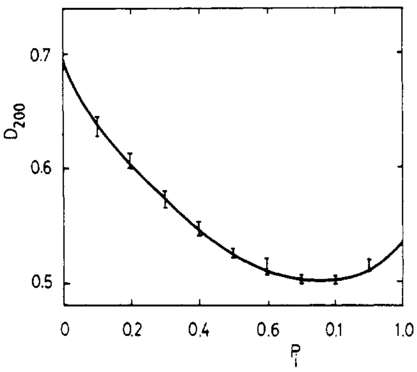

Figure 2. Theoretical values of D_{200} as a function of the isotactic fraction P_i at T = 300 K.

Table IV
Variation of D_{200} with Energetic Parameters and Temperature, Written As $10^2\ \delta \ln (D_{200})/\delta$(parameter)

parameter	$P_i = 0$	$P_i = 0.5$	$P_i = 1.0$
E_η	−1996.4	−670.9	30.6
E_ω		47.7	70.3
$E_{\omega'}$	572.6	126.4	
$E_{\omega''}$		−150.0	99.5
T	−4.9	−1.0	−0.5

Table V
Statistical Weights and Probabilities of Occurrence of Each Conformation $|\chi,\xi|$ for PCS[a] and PVK[b] at T = 300 K

	conformation $\lvert\chi,\xi\rvert$		
	tt	tg = gt	gg
	Statistical Weights		
meso PCS	0.046	0.642	0.019
meso PVK	0.093	0.392	0.024
racemic PCS	1	0.029	0.412
racemic PVK	1	0.136	0.154
	Probability of Occurrence		
meso PCS	0.133	0.432	0.003
meso PVK	0.238	0.377	0.008
racemic PCS	0.784	0.017	0.182
racemic PVK	0.757	0.083	0.077

[a] Identical for PS, PCS, and PBS. Taken from ref 10–13. [b] Taken from ref 2.

the conformations on the polarity of the chains.

Let us examine the syndiotactic chain first. As in the case of PCS, the preferred conformation of PVK is the planar all trans, although the preference is slightly smaller in PVK than in PCS. However, the main difference between both polymers is that in the case of PCS the incidence of |gt| or |tg| conformations is almost negligible so that the |tt|tt|... sequence is mainly disrupted by a |gg| conformation which produces two segments whose dipole moments cancel out (disregarding the distortion of geometry). On the contrary, in PVK, |tg|, |gt|, and |gg| have almost the same probability of occurrence, so that a |tt|tt|... sequence may be interrupted by any of these three conformations with, roughly, the same probability. The cancellation of the dipole moment of two |tt|t... segments separated by either |tg| or |gt| is not as complete as when they are separated by |gg|. Consequently, the correlation between dipole moments of successive |tt|t... sequences is adverse ($D < 1$) but not as much as in the case of PCS (D_x(PVK) > D_x(PCS)).

Table IV shows that the value of D_∞ of the syndiotactic chain (i.e., $P_i = 0$) is very sensitive to E_η and decreases as E_η increases (i.e., as η decreases). An increase in E_η will increase the incidence of both |tg| and |gt| conformations (that depend on $1/\eta$), and especially that of |gg| which depends on $1/\eta^2$, thus enhancing the cancellation between dipole moments of successive |tt| sequences and therefore decreasing the value of D_x.

The variation of D_x with $E_{\omega'}$ is much smaller and has the opposite sign than that of E_η. An increase in $E_{\omega'}$ decreases the incidence of |tg| and |gt| and increases those of |tt| and |gg|. For instance, an increase of 0.1 kcal/mol in $E_{\omega'}$ decreases |tg| and |gt| by about 12% each, increases |tt| by about 2% and increases |gg| by about 3.9%. Those variations in the probability of occurrence have opposite effects on D_x; thus, whereas the increase in |tt| and the decrease in |gt| and |tg| tend to raise the value of D_x, the increase in |gg| tends to diminish it. As Table IV shows, the effects tending to increase D_x dominate those tending to decrease it; consequently, D_x increases with $E_{\omega'}$, although the variation is much smaller than with E_η. The variation of D_x with both E_η and $E_{\omega'}$ gives negative contributions to its temperature coefficient; this magnitude is therefore negative and large in absolute value.

We focus now on the isotactic chain. As Table V shows, the preferred conformations of meso dyads in PVK are |tg| or its enantiomorph |gt|, that generates a 3_1 helix disrupted by |tt|, and only occasionally by |gg| (although the |gg| conformation of bonds i and $i + 1$ meeting at the C^α atom is forbidden). The main difference between PCS and PVK lies in the relative incidence of |tg| or |gt| vs. |tt| conformations. Thus, while in PCS the average length of |tg| or |gt| sequences is larger than 3, so that at least one turn of the helix is generated before the sequence is disrupted, and therefore there is a net resultant of the dipole moment along the axis of the helix. In the case of PVK the average length is smaller than 3; thus not even a turn is completed when the helix is interrupted. The cancellations are therefore much stronger, and as a consequence, the calculated value of D_x is much smaller for PVK than for PCS.

The effect of a change in the energetic parameters is much smaller in the case of the meso than in that of racemic. It is noteworthy that all the variations are positive (i.e., D_x increases with increasing energies), since an increase in any of these energies means to increase the preference for |tg| or |gt| conformations and therefore to improve the formation of helix sequences.

Since the variations of D_x with the energies are not large, the contributions to the temperature coefficient are small; moreover, the contribution from E_η is positive whereas those of the other energies are negative. As a consequence, the temperature coefficient of D_x is much smaller in absolute value than in the case of the syndiotactic chain.

Comparison of Theory and Experiment

Studies carried out on vinyl polymers obtained by free radical polymerization suggest that the stereochemical composition of most of these polymers is slightly syndiotactic.[15,16] The analysis of the ^{13}C NMR spectrum of PVK indicates that the isotacticity of these chains is ca. 0.33, and consequently, the comparison between theory and experiments will be made for chains with this stereochemical composition. According to theory, the dipole moment of PVK should be moderately dependent on the stereochemical composition of the chains. The values of D_x are 0.69 and 0.53 for chains in which the meso dyad fraction is 0 and 1, respectively. For chains about 33% isotactic, D_x = 0.56, in reasonable agreement with the experimental result (0.41) obtained for PVK. The theory suggests a negative temperature dependence for the dipole moments of these chains in opposition to the experiments in which a positive dependence has been found. The disagreement between theory and experiment in this case may be attributed either to specific solvent effects or to errors involved in the experimental determination of the dipole moments. It should be stressed in this regard that the temperature coefficients are in general small quantities corresponding to changes of only a few tenths percent per degree, and consequently, serious errors may be involved in their determination.

Registry No. PVK (homopolymer), 25067-59-8.

References and Notes

(1) Penwell, R. C.; Ganguly, B. N.; Smith, T. W. *J. Polym. Sci., Macromol. Rev.* **1978**, *13*, 63.
(2) Sundararajan, P. R. *Macromolecules* **1980**, *13*, 512.
(3) Barrales-Rienda, J. M.; Galera Gômez, P. A.; Gonzalez Ramos, J.; Otero Aenlle, E. *An. Quim.* **1980**, *76*, 49.
(4) Kawamura, T.; Matsuzaki, K. *Makromol. Chem.* **1978**, *179*, 1003.
(5) Terrel, D. R.; Evers, F. *Makromol. Chem.* **1982**, *183*, 863.
(6) Riande, E. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 2331.
(7) Guggenheim, E. A. *Trans. Faraday Soc.* **1949**, *45*, 714; **1951**, *47*, 573. Smith, J. W. *Trans. Faraday Soc.* **1950**, *46*, 394.
(8) North, A. M.; Phillips, P. *Chem. Commun.* **1968**, *21*, 1340.
(9) Blasco, F.; Riande, E. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 835.
(10) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.
(11) Saiz, E.; Mark, J. E.; Flory, P. J. *Macromolecules* **1977**, *10*, 967.
(12) Suter, U. W.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 152.
(13) Saiz, E.; Suter, U. W.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2*, **1977**, *77*, 1538.
(14) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.
(15) Bovey, F. A. "High Resolution NMR of Macromolecules"; Academic Press: New York, 1972.
(16) Pino, P.; Suter, U. W. *Polymer* **1976**, *17*, 977.

Intrinsic Viscosity of Poly(hexyl isocyanate) in Butyl Chloride

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ABSTRACT: Zero-shear-rate intrinsic viscosities [η] of poly(hexyl isocyanate) (PHIC), a typical semiflexible polymer, in butyl chloride at 25 °C were determined for 31 fractions ranging in weight-average molecular weight from 4×10^3 to 7×10^6. The measured values of [η] indicated the chain conformation of PHIC to change continuously from a short rod to a long coil with an increase in molecular weight and could be fitted accurately by the Yamakawa–Fujii–Yoshizaki theory for unperturbed wormlike cylinders (Kratky–Porod chains) provided that the values of 760 nm^{-1}, 35 nm, and 1.5 nm were assigned to the molar mass per unit contour length, persistence length, and diameter of the PHIC chain, respectively.

Introduction

Poly(hexyl isocyanate) (PHIC) is known as a typical semiflexible polymer.[2,3] In a previous paper,[4] it was shown that the dimensions and particle scattering function of this polymer in hexane can be described accurately by an unperturbed Kratky–Porod wormlike chain. Thus, PHIC should be useful as a model polymer for checking hydrodynamic theories on unperturbed wormlike chains.

In the present study, 31 PHIC fractions covering a wide range of molecular weight were examined by viscometry, with butyl chloride chosen as the solvent, and the zero-shear-rate intrinsic viscosities [η] obtained were compared with the Yamakawa–Fujii–Yoshizaki theory[5,6] for unperturbed wormlike cylinders.

Experimental Section

Preparation of Low Molecular Weight Samples. Previous investigators[7-9] found that poly(alkyl isocyanates) in carbon tetrachloride (CCl_4) containing a small amount of a strong acid such as trifluoroacetic acid (TFA) undergo degradation. To take advantage of this finding to prepare samples of lower molecular weights, we examined the degradation of high molecular weight PHIC in mixtures of CCl_4 and TFA.

Figures 1 and 2 show the changes in $(\ln \eta_r)/c$ with time that occurred following the addition of TFA to CCl_4 solutions. Here, η_r is the relative viscosity and c, the polymer mass concentration. It can be seen from Figure 1 that 30% TFA rapidly fragments PHIC of different chain lengths to nearly equal shorter chains. In Figure 2, the rate of degradation for a sample (viscosity-average molecular weight $M_v = 1.7 \times 10^5$) is seen to depend strongly on TFA composition.

On the basis of these data, we chose the composition of TFA and the duration of exposure to the mixed solvent suitable for degrading high molecular weight PHIC samples ($10^5 \lesssim M_v \lesssim 5 \times 10^6$) and obtained seven shorter chain products. The degraded products were washed with methanol, water, and acetone and freeze-dried from benzene solutions. Elemental analysis showed no difference in chemical composition between the purified degraded and undegraded original samples.

Each of the degraded samples was divided into several parts by repeating fractional precipitation with CCl_4 as the solvent and methanol as the precipitant. Twelve fractions designated below as f-1, f-2, ..., f-12 were chosen, reprecipitated from CCl_4 solutions into methanol, and freeze-dried from benzene solutions. The high molecular weight fractions (F-1, F-2, ..., F-19) prepared in our previous work[4] were added to these fractions.

Sedimentation Equilibrium. The weight-average molecular weights M_w of fractions f-1, f-2, ..., f-12 were determined by sedimentation equilibrium in a Beckman Model E ultracentrifuge with butyl chloride at 25 °C as the solvent.[10] A Kel-F 12-mm double-sector cell was used, and the liquid column was adjusted to 1.5–2.0 mm. The rotor speed ranged from 15000 to 30000 rpm depending on the fraction studied.

The solvent butyl chloride (Wako Pure Chemicals) was fractionally distilled over calcium chloride. The partial specific volume of PHIC in this solvent at 25 °C was determined to be 0.952 cm^3 g^{-1}, with fractions f-3, f-7, and f-8 used for the measurements. This value is very close to 0.950 cm^3 g^{-1} determined previously[4] for high molecular weight PHIC in hexane. The density of butyl chloride at 25 °C was 0.91272 g cm^{-3}.

The specific refractive index increment of PHIC in butyl chloride at 25 °C for 546-nm wavelength was 0.0916 cm^3 g^{-1}, independent of the molecular weight of the polymer.

Viscometry. Viscosities of high molecular weight fractions F-5, F-6, ..., F-19 in butyl chloride at 25 °C were measured at shear rates G lower than 1 s^{-1}, using a rotational viscometer of the Zimm–Crothers type.[11] The measured $(\ln \eta_r)/c$ were equated to the zero-shear-rate values, since they were independent of G.