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Global conformations of chiral polyisocyanates in dilute solution

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Abstract

Global conformations of chiral polyisocyanates were discussed in terms of light scattering and viscosity data collected for stereospecifically deuterated poly(hexyl isocyanate)s, poly((*R*)-2,6-dimethylheptyl isocyanate) (PNIC), and copolymers of hexyl isocyanate (HIC) with (*R*)-2,6-dimethylheptyl isocyanate (NIC). The light scattering data and viscosity data obtained were analyzed consistently in the framework of the worm-like chain model. The persistence length q was the same for PHIC and deuterated PHIC, but increased with the mole fraction of NIC in the HIC–NIC copolymers, e.g. from 41 to 56 nm in hexane at 25°C. The results were not detailed enough to substantiate the broken worm model in line with the helix reversal model of Lifson et al. Gel permeation chromatographic behavior of the polyisocyanates was also examined, so that it could be used for the determination of the molecular weight distribution of a sample with a very minute amount (at most 1 mg or less). © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Conformation; Worm-like chain; Persistence length

1. Introduction

Polyisocyanates consisting of consecutive amide bonds are known to be typical semiflexible polymers in dilute solution, and their global properties are well represented by the worm-like chain of Kratky and Porod [1–9]. It is well established that their semiflexibility comes from their amide bonds of partial double bond nature, which, arranged in coplanar conformation, would form a long conjugated system, but steric hindrance between the backbone and side-chain prohibits the backbone to have the planar conformation and distorts it into a helical conformation. Indeed the helical conformation was found for poly(butyl isocyanate) in the solid state by X-ray analysis [10] and predicted by conformational analysis [3,11–16]. These studies suggest that many polyisocyanates have essentially the same helical conformation, although the sense of the helix differs for different polymers. In an archiral polyisocyanate both left-handed and right-handed helices coexist in equal proportion, whereas this symmetry in helix sense is broken for polyisocyanates undergoing chiral perturbations. Indeed this symmetry break gives rise to extraordinarily large optical activity in chiral polyisocyanates [17–19].

A series of investigations on this optical activity [20–24] show that the two helices of the opposite senses coexist on the same chain in different proportions, namely a polymer chain consists of an alternating sequence of the left-handed and right-handed helices with helix breaks or reversals in between. This picture of polyisocyanate chain, leading to a broken chain, appears to contradict with the continuous worm-like chain model well accepted for polyisocyanates. This problem has been discussed already by previous investigators, but with the results depending on polymer or method employed [3,12–16,25–27]. Here we revisit this problem by summarizing the information found in the literature along with light scattering and viscosity data collected recently for stereospecifically deuterated poly(hexyl isocyanate)s and poly((*R*)-2,6-dimethylheptyl isocyanate) and copolymers of hexyl isocyanate with (*R*)-2,6-dimethylheptyl isocyanate. Actually we try to analyze the collected light scattering and viscosity data in the framework of the worm-like chain model.

We also discuss gel permeation chromatography behavior of chiral polyisocyanates, which must be closely related to their global properties, because this information was needed in recent studies on chiral polyisocyanates to determine the

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molecular weight distributions of fractionated samples, whose amounts were too small to be amenable to any other method.

2. Experimental

2.1. Polymer samples

Nine as polymerized samples of chiral polyisocyanates were chosen from the stock at Polytechnic University. They were coded as follows: poly(1-deuterio-*n*-hexyl isocyanate) (α PdHIC) as αHM and α170, poly(2-deuterio-*n*-hexyl isocyanate) (β PdHIC) as β250, poly((*R*)-2,6-dimethylheptyl isocyanate) (PNIC) as N15, and copolymers of hexyl isocyanate (HIC) and (*R*)-2,6-dimethylheptyl isocyanate (NIC) as NH$x/y$, where y and x stand for the mol% of the former and latter monomer units, respectively, in each copolymer. Two lower-molecular-weight αPdHIC samples, α104 and α40, and two βPdHIC samples β50 and β20 were obtained by degrading original samples with trifluoroacetic acid (TFA). A typical procedure was as follows. TFA at *ca.* 20 wt% in chloroform was added dropwise to a 10 ml chloroform solution of *ca.* 20 mg of an original sample in a Ubbelohde viscometer, and the degradation was monitored by measuring $(\ln \eta_r)/c$, where η_r is the relative viscosity and c is the polymer mass concentration of the solution; $(\ln \eta_r)/c$ was taken as the measure of molecular weight. The addition of TFA was continued until the solution showed a desired viscosity value, and then the reaction was terminated by triethylamine. The resulting polymer was recovered by pouring the solution into a large excess of methanol, washed with water and methanol, and dried under vacuum. All the degraded samples for the present study were obtained in this way.

The original and degraded polymer samples except for β250 were divided into three parts by fractional precipitation with benzene as the solvent and methanol as the precipitant, and each central fraction was used for the present study.

2.2. Solvents and solutions

Hexane and toluene were dried and refluxed 4 h over metal Na and then purified by distillation. Similarly dichloromethane and 1-chlorobutane were distilled from CaH_2. Usually commercial chloroform contains a small amount of ethanol as stabilizer, which may differ for different batches. Therefore, chloroform used for viscosity measurement was purified as follows. To commercial chloroform, a 10%(wt) of concentrated sulfuric acid was added and stirred for 2–3 days. After sulfuric acid was removed by decantation, the EtOH-free chloroform was placed in a separatory funnel and washed with 1 N NaOH once and with distilled water until the aqueous layer became neutral. The obtained chloroform was dried over $CaCl_2$ for 12 h, and then distilled. The purified chloroform with 0.35% EtOH by weight added, was used as the solvent for viscosity measurements.

Weighed amounts of a given polymer sample dried in vacuum overnight and a solvent were mixed in a ground-glass-stoppered Erlenmeyer flask at room temperature. For toluene, chloroform, and dichloromethane solutions, the polymers were completely dissolved after being stirred for about one day at room temperature. In the case of solutions in hexane and 1-chlorobutane, on the other hand, the stirring had to be continued for 3–7 days at 40°C for complete dissolution.

2.3. Light scattering measurements

Light scattering measurement was carried out for 10 optically active polyisocyanate samples in hexane at 25°C (cf. Table 1). For each sample, hexane solutions of five different concentrations were prepared. The polymer solutions and the solvent hexane were made optically clean by centrifugation at a rate of $1.2 \times 10^4\, \boldsymbol{g}$ for 2 h in a Sorvall Type RC2-B centrifuge. Then each solution was directly transferred into a light scattering cell with a pipette; both the cell and pipette had been rinsed with refluxing acetone vapor for about 10 h and dried. A Fica-50 light scattering photometer was used to measure the scattered intensities at scattering angle θ between 13°–150° for vertically polarized light of 436 and 546 nm wavelengths with no analyzer. The instrument was calibrated with pure benzene as the reference liquid with the Rayleigh ratio of $46.5 \times 10^{-6}\ cm^{-1}$ at 546 nm [28]. Previous procedures [5,29,30] for experiment and data analysis were followed, which would guarantee the credibility of the results derived.

2.4. Specific refractive index increment

In order to analyze the light scattering data, the specific refractive index increment ($\partial n/\partial c$) is required. Its values for various samples in hexane at 25°C were measured on a Schulz–Cantow-type differential refractometer. The $\partial n/\partial c$ values for αPdHIC and βPdHIC at wavelengths 436 and

Table 1
Results from light scattering measurements on polyisocyanates in hexane at 25°C

Sample	M_W (10^5)	$\langle S^2\rangle_z$ (10^{-10} cm^2)	A_2 (10^{-3} cm^3 g^{-2} mol)
α104	10.4	2.14	0.85
α40	4.03	0.74	1.08
αHM	19.5	4.02	0.70
β250	25.1	5.13	1.02
β50	5.13	1.00	1.20
β20	2.22	0.32	1.08
N15	1.45	0.18	0.84
NH37/63	14.2	3.08	0.93
NH15/85	19.0	3.98	1.26
NH4/96	6.66	1.32	0.75

546 nm are shown to be 0.134(± 0.0015) and 0.129 (± 0.005) $\mathrm{cm}^3\,\mathrm{g}^{-1}$, respectively. These values agree precisely with those for PHIC in hexane solution [5]. On the other hand, the $\partial n/\partial c$ values for the copolymers and PNIC are lower than these values, decreasing with the mole fraction x of NIC in the copolymers. They are expressed by

$$\frac{\partial n}{\partial c} = 0.1340 - 0.0116x \text{ (at 436 nm)}$$

$$\frac{\partial n}{\partial c} = 0.1290 - 0.0089x \text{ (at 5436 nm)}$$

The deviation of the measured values from these relations is about 2%–5%.

2.5. Viscometry

Zero-shear-rate viscosities for polymer samples were measured in the following solvents: hexane at 25°C, toluene at 10°C, 25°C and 40°C, 1-chlorobutane at 25°C, chloroform at 25°C, and dichloromethane (DCM) at 20°C. A low-shear four-bulb capillary viscometer was used for the high molecular weight samples ($M_w > 2 \times 10^5$), whereas conventional capillary viscometers of the Ubbelohde type were used for the low molecular weight samples. Intrinsic viscosities $[\eta]$ and Huggins viscosity constant k' were estimated by using Huggin's, Mead-Fouss', and Billmeyer's plots.

2.6. Gel permeation chromatography (g.p.c.)

For gel permeation chromatography (g.p.c.) use was made of an analytical gel permeation chromatograph TOSOH HLC8020 equipped with a u.v. detector operating at 254 nm under the following operating conditions: two TOSOH columns TSK G5000HxL and TSK G4000HxL

Table 2
Results from viscosity measurements on polyisocyanate samples

Sample	Solvent	T (°C)	$[\eta]$ ($10^2\ \mathrm{cm}^3\,\mathrm{g}^{-1}$)	k'
α104	*n*-Hexane	25	46.5	0.50
	1-Chlorobutane	25	34.3	0.45
	DCM	20	18.7	0.48
	Toluene	25	37.4	0.48
β250	*n*-Hexane	25	86.8	0.48
	1-Chlorobutane	25	64.0	0.50
	Chloroform	25	41.2	0.47
	DCM	20	36.9	0.41
	Toluene	10	78.0	0.49
		25	71.5	0.50
		40	59.7	0.48
β50	*n*-Hexane	25	22.6	0.36
	DCM	20	9.9	0.39
	Toluene	10	22.7	0.44
		25	20.1	0.54
		40	18.5	0.43
β20	*n*-Hexane	25	10.3	0.39
	DCM	20	5.3	0.48
	Toluene	10	9.2	0.41
		25	8.5	0.42
		40	7.6	0.44
N15	*n*-Hexane	25	4.03	0.30
	Chloroform	25	2.97	0.46
NH37/63	*n*-Hexane	25	53.8	0.46
	1-Chlorobutane	25	50.1	0.46
	DCM	20	27.3	0.44
	Toluene	10	49.9	0.38
		25	46.6	0.40
		40	41.4	0.44
NH15/85	*n*-Hexane	25	66.6	0.44
	Toluene	10	55.2	0.42
		25	50.6	0.35
		40	44.8	0.42
NH4/96	*n*-Hexane	25	29.5	0.46
	1-Chlorobutane	25	20.2	0.45
	DCM	20	13.3	0.45
	Toluene	10	23.1	0.45
		25	20.5	0.45
		40	19.5	0.45

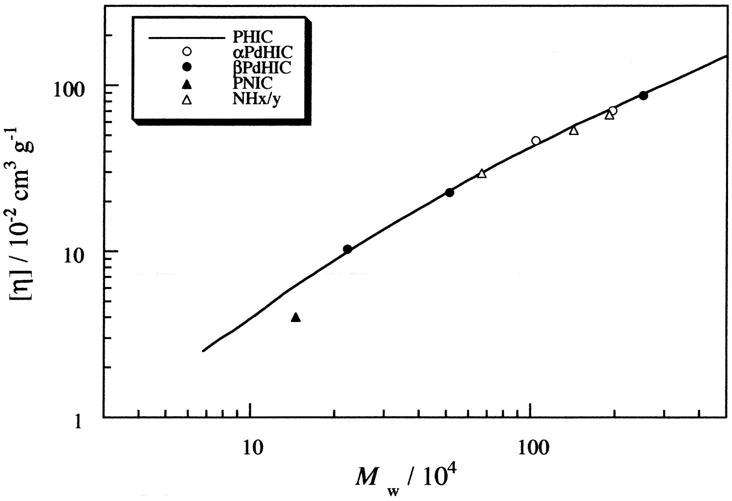


Fig. 1. Molecular weight dependence of intrinsic viscosity for polyisocyanates in hexane at 25°C. Symbols, experimental data for different polyisocyanates; curve, experimental values for PHIC, which is indistinguishable from theoretical values calculated by the Yamakawa–Yoshizaki–Fuji theory.

connected in series with chloroform at 40°C as the eluent; the polymer concentration was about 1×10^{-5} g cm^{-3}, the injection volume was 0.1 cm^3, and the flow rate was 1 cm^3 min^{-1}.

3. Results

Generally speaking light scattering data from a copolymer have to be corrected for composition heterogeneity if the constituent monomer units differ in refractive index increment $\partial n/\partial c$. The difference in $\partial n/\partial c$ between PHIC and PNIC is rather small, being about 0.01 or less than 10% as shown in Section 2, and hence the change in $\partial n/\partial c$ for NH*x*/*y* with copolymer composition is only gradual. Therefore, we analyzed light scattering data for these copolymers without considering the heterogeneity correction. All the light scattering data obtained are summarized in Table 1. Their credibility may be guaranteed by the use of the previous procedures [5,29,30]. It is seen that the values of A_2 are about 1.0×10^{-3} cm^3 g^{-2} mol^{-1}, which scatter around the values reported for PHIC in the same solvent [5], indicating that hexane is a good solvent for these polymers as naturally expected from their chemical structures in comparison with PHIC.

Table 2 presents the intrinsic viscosities $[\eta]$ along with the Huggins viscosity constant k' obtained, where $[\eta]$ is expressed in units of 10^2 cm^3 g^{-1}. Figs 1 and 2 compare, respectively, the molecular weight dependence of $[\eta]$ in hexane at 25°C and in toluene at 25°C of the present polymers along with those of PHIC reported previously [5,7], where the latter data are represented by smooth curves. In both solvents, the data points for αPdHIC and βPdHIC (circles) appear plotted precisely on the PHIC curves, whereas for N15 (PNIC) and NH*x*/*y* tend to deviate more or less below the PHIC curves.

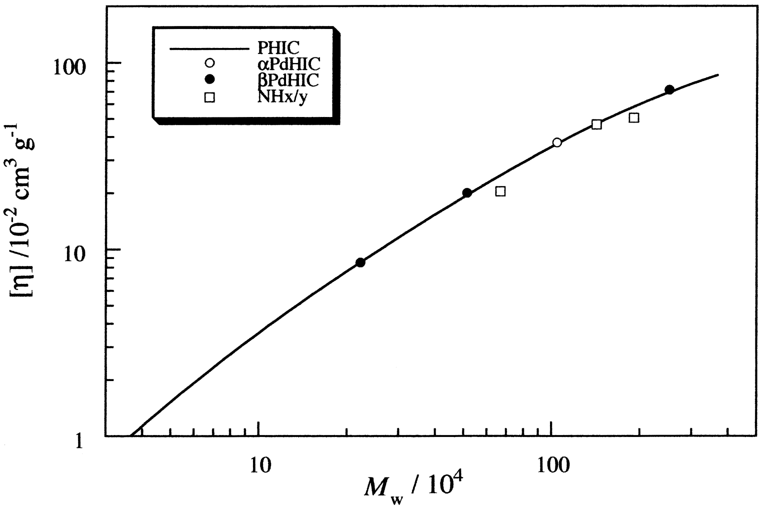


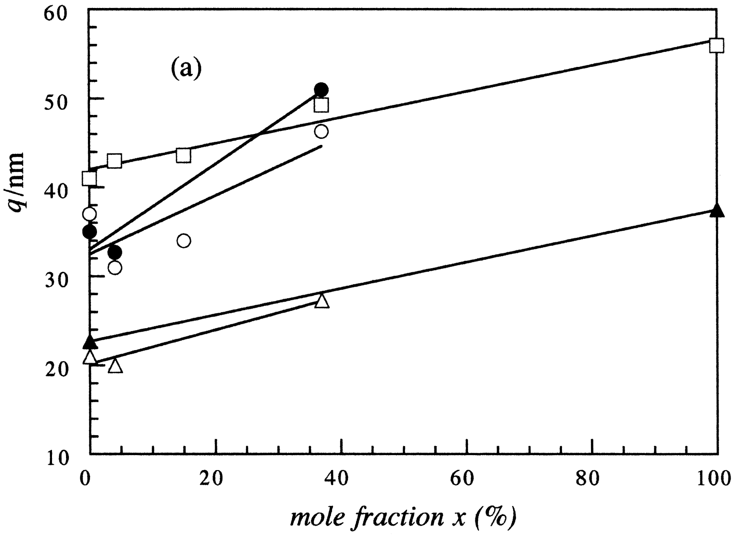
Fig. 2. Molecular weight dependence of intrinsic viscosity for polyisocyanates in toluene at 25°C. Symbols, experimental data for different polyisocyanates; curve, experimental values for PHIC, which is indistinguishable from theoretical values calculated by the Yamakawa–Yoshizaki–Fuji theory.

4. Discussion

4.1. Global conformations

It is well established that the conformation of poly(hexyl isocyanate) in solution can be expressed by the worm-like chain model [5–9]. Therefore, we examine whether this is also true for the present polyisocyanates. According to the theory of Yamakawa and Fujii [31], and Yamakawa and Yoshizaki [32], the intrinsic viscosity $[\eta]$ of a worm-like cylinder is a function of the contour length L, the diameter d and the persistence length q of the cylinder, where L is related to its molecular weight M by $L = M/M_L$, with M_L being the mass per unit length. The theory is tested in Figs 1 and 2, where the solid curves represent the values of $[\eta]$ for PHIC at 25°C in hexane and in toluene, respectively, which are almost indistinguishable from the corresponding theoretical curves with the parameter values given in the literature [5–9]. It can be seen that the data points for αPdHIC and βPdHIC (circles) follow these curves closely. Since the chemical structures of these polymers are the same as that of PHIC except that one deuterium atom is replaced by a hydrogen atom, it is a very good approximation to assign the same values of M_L and d for these polymers. Then we are left with only one parameter q for the deuterated polymers to be adjusted. Thus we are led to conclude that these polymers have the same q, and hence characterized by the same worm-like cylinder parameters, M_L, d and q, as those for PHIC in these solvents.

On the other hand, those for PNIC and copolymers of NIC and HIC are not precisely fitted by the PHIC curves. Thus it follows that their conformations are different from that of PHIC when compared in the same solvent. We will determine their worm-like cylinder parameters in the following way. Since all these polymers have the same backbone, it is reasonable to assume that M_L is related to the average



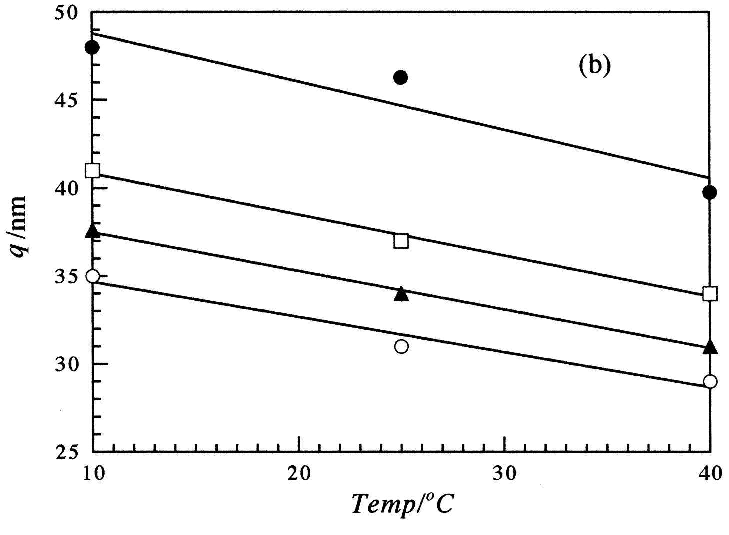


Fig. 3. Persistence length for NH$x/y$ in the indicated solvents. (a) Composition dependence symbols: □, hexane; ○, toluene; ●, 1-chlorobutane; ▲, chloroform at 25°C; △, dichloromethane at 20°C. (b) Temperature dependence symbols: ●, NH37/63; □, PHIC in toluene; ▲, NH15/85; ○, NH4/96 in toluene. Solid lines, eye-guides.

monomer molecular weight M_O by

$$M_L = (M_O/M_{O,\mathrm{PHIC}})M_{L,\mathrm{PHIC}} \qquad (1)$$

where the quantities with the subscript 'PHIC' refer to PHIC. For simplicity we also assume that the specific volume is the same for all the polymers to obtain the diameter d of the cylinder as

$$d = d_{\mathrm{PHIC}}(M_O/M_{O,\mathrm{PHIC}})^{1/2} \qquad (2)$$

With these M_L and d values assumed, we sought the values of the remaining parameter q which would give the best fit between the observed and calculated $[\eta]$ values for all the data in Table 2. The accuracy of the q values obtained is only moderate because of the above assumptions. The dependence of q on the mole fraction x (in%) of NIC and temperature in various solvents are shown in Fig. 3, where those at $x = 0$ are the literature values [5–9]. It is seen in Fig. 3a that q increases more or less linearly with increasing NIC content and differs for different solvents for every polymer examined, with that for PNIC being the maximum. Fig. 3b shows that for every NH$x/y$ studied q decreases almost linearly with temperature as does the q of PHIC in toluene [7]; the decrease amounts to about 20% between 10°C and 40°C.

The mean-square radius of gyration $\langle S^2\rangle$ of a worm-like chain is expressed as [33]

$$\langle S^2\rangle = qL/3 - q^2 + (2q^3/L)[1-(q/L)(1-e^{-L/q})] \qquad (3)$$

Therefore, $\langle S^2\rangle/L^2$ is a unique function only of $L/2q$. Fig. 4 is constructed to test this prediction as the plot of $\langle S^2\rangle_z/L_w^2$ against $L/2q$ for the data in Table 1 along with the q values obtained earlier from the viscosity data, where the solid curve represents theoretical values for $\langle S^2\rangle/L^2$ calculated by Eq. (3). The data points are seen to deviate significantly upward the curve, scattering around the dashed curve, which represents $1.2\langle S^2\rangle/L^2$, with that for N15 deviating furthermore. This deviation is due to the polydispersity of our samples, which were only crudely fractionated; the polydispersity index M_w/M_n for each sample was in the range between 1.07 and 1.2 but no accurate information was obtained about M_z and M_{z+1}. It is noted, on the other hand, the polydispersity may have no serious effect when intrinsic viscosity data are analyzed with the weight-average molecular weight, and hence the above analysis of the viscosity data is considered correct.

Green et al. [25] found from light scattering data that poly((*S*)-2,2-dimethyl-1,3-dioxolane-4-methylene isocyanate) has an extended conformation compared with the corresponding (*RS*)-polymer, i.e. q is 60 and 25 nm, respectively, for these polymers. They ascribed this difference to more frequent helix reversals for the (*RS*)-polymer than for the (*S*)-polymer, favoring the broken worm picture for the former [25,26]. It is, however, difficult to generalize this conclusion to other polyisocyanates, because this is a special case, where these polymers have a large side-chain, 2,2-dimethyl-1,3-dioxolane which would prohibit dynamic helix reversal; the helix reversal may be static, remaining as polymerized.

The conformational analyses [13,16] provide the possibility of the broken worm due to helix reversal, but the continuous worm can be also consistent with the conformational calculation and spectroscopic data. In this connection it is clear that only the viscosity and light scattering data are too crude to differentiate continuous and broken worms. In a series of studies on chiral polyisocyanates [20,23,24], we have shown that helix reversal is the essential feature of the conformation of polyisocyanate chain, which would be most frequent for the achiral limit. Taken literally, this means that the chain dimension would be minimum at the achiral limit. As shown earlier, this is not the case with αdHIC/HICx/y and βdHIC/HICx/y, where q is independent of chirallity. As shown in Fig. 3, q of NIC–HIC copolymers does not show remarkable disproportionate change with x, which is contrasted with remarkably non-linear dependence of the optical rotation (or the chiral conformation) of the copolymer on the monomer content [19,34]. This difference throws doubt on the causality between the helix reversal and chain stiffness of the NIC–HIC copolymers. Indeed it is

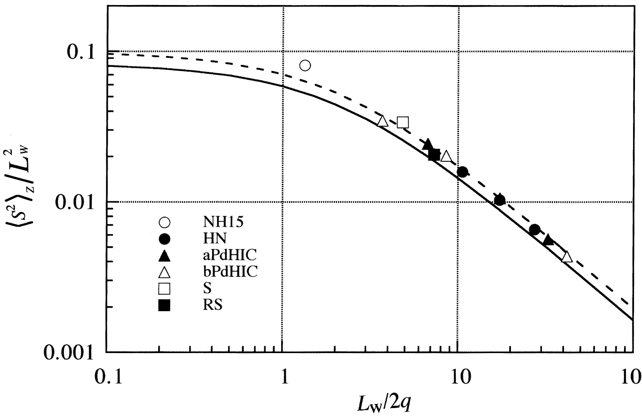


Fig. 4. Plot of $\langle S^2\rangle_z/L_w^2$ against $L_w/2q$ in hexane at 25°C. Symbols, experimental data for different polyisocyanates: □, poly((*S*)-2,2-dimethyl-1,3-dioxolane-4-methylene isocyanate); ■, poly((*RS*)-2,2-dimethyl-1,3,-dioxolane-4-methylene isocyanate) [25]; solid curve, values for $\langle S^2\rangle/L^2$ calculated by Eq. (3); dashed curve, $1.2\langle S^2\rangle/L^2$.

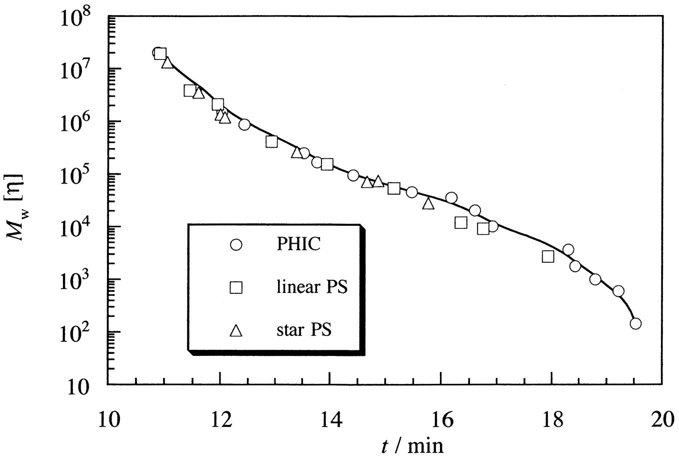


Fig. 5. Universal calibration curve for g.p.c. analysis. Symbols: ○, PHIC; □, linear polystyrene; △, four-arm star polystyrene.

difficult to explain the large difference in [η] for N15 between hexane and chloroform; this sample has less than one helix reversal per chain [35]. Thus we conclude that the increase in chain stiffness of NIC–HIC copolymers with increasing chiral NIC monomer content does not necessarily indicate the predominant importance of the helix reversal in the global chain conformation, because the bulky side-chain of the NIC monomer unit may restrict also local fluctuations about the preferred energy minima in main-chain bond torsion and angles, which is another factor determining the chain stiffness. A possible explanation may be to consider that the helix reversal, which appears itself in such a local static average as optical rotation, is a fast dynamic process smearing out the broken-rod nature of the polymer chain.

4.2. Gel permeation chromatography

Gel permeation chromatography (g.p.c.) is based on the size-exclusion occurring when a polydisperse polymer is eluted through a column packed with porous particles. It is known that for flexible polymers the retention time or elution volume is related to the product $M[\eta]$. Fig. 5 tests this empirical relation among linear and four-arm star polystyrenes and PHIC using well-characterized samples (M Okumoto, K Terao, Y Nakamura, T Norisuye, A Teramoto, unpublished results) and Ref. [36]. It is surprising that all the data points including those for PHIC form a composite curve, i.e. a universal calibration curve, conforming to the above premise. It was shown previously [23] that a calibration curve for PHIC constructed with a number of reference samples of known molecular weights from our stock so that their M_W were reproduced with 3% was valid also for a fractionated sample of βPdHIC, whose M_W was determined by low-angle laser light scattering. Therefore, it is reasonable to assume that both αPdHIC and βPdHIC can be characterized by the same calibration curve.

We have no g.p.c. reference sample for other polyisocyanates. Therefore, we rely on the above universality to circumvent this difficulty and assume the following equality valid at a given elution time t:

$$M(t)[\eta](t) = M_{\mathrm{PHIC}}(t)[\eta]_{\mathrm{PHIC}}(t) \tag{4}$$

With the equality, the molecular weight of a particular polymer eluting at t $M(t)$ is related to that of PHIC, $M_{\mathrm{PHIC}}(t)$ by

$$\begin{aligned}\gamma_\eta(t) &= \frac{M(t)}{M_{\mathrm{PHIC}}(t)} = \frac{[\eta]_{\mathrm{PHIC}}(t)}{[\eta](t)} \\ &= \frac{f(M_{\mathrm{L,PHIC}}(t), q_{\mathrm{PHIC}}, d_{\mathrm{PHIC}}, M_{\mathrm{PHIC}}(t))}{f(M_{\mathrm{L}}, q, d, \gamma_\eta(t) M_{\mathrm{PHIC}}(t))}\end{aligned} \tag{5}$$

Here f is given by the theory of Yamakawa and Yoshizaki, and Yamakawa and Fuji as a function of M_{L}, q, d and $M(t)$ of the polymer. Thus if the values of M_{L}, q and d for both PHIC and the particular polymer are known along with $[\eta](t)$, $\gamma_\eta(t)$ can be determined by solving Eq. (5), consequently from $M(t)$ from $M_{\mathrm{PHIC}}(t)$. We will use this idea to determine the molecular weights of fractionated PNIC and NH*x*/*y* samples, whose amounts are too minute (at most 1 mg or less) to be amenable to usual methods [35].

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