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Hydrodynamic Properties and Unperturbed Dimensions of Polydecahydro-β-naphthyl and Poly-β-naphthyl Methacrylates in Different Solvents

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ABSTRACT

Intrinsic viscosity, sedimentation, light-scattering, and osmotic-pressure measurements have been carried out at 25° on dilute solutions of polydecahydro-β-naphthyl methacrylate (PDNa) and of poly-β-naphthyl methacrylate (PNa). For both polymers, the degree of polydispersity was around 1.5 and the molecular weight range was large: 10^5 to 3×10^6. Relations between $[\eta]$, $[S_0]$, A_2, and molecular weight have been established.

The applicability of the different theories (Stockmayer-Fixman, Kurata-Stockmayer, Fox-Flory, Cowie, Berry, Kamide-Moore) for the determination of the unperturbed dimensions from the viscosity data is discussed; Berry's relation best fits the experimental data.

These dimensions, calculated from the sedimentation data according to the Cowie-Bywater relation, agree with those obtained by viscosity. The flexibility factor σ is 2.9 for PDNa and 3.1 for PNa. These large values are a consequence of the presence of very bulky groups in the side chain; however, the higher σ value for PNa led to the assumption that a specific interaction between the aromatic rings influences the rigidity of the main chain.

INTRODUCTION

In this paper, we describe the hydrodynamic behavior in solution of two closely related polymers: polydecahydro-β-naphthyl and poly-β-naphthyl methacrylates.

The configuration of the latter polymer in benzene at 21° has been determined by Berdnikova et al. [1] from viscosity, sedimentation, and diffusion measurements; the flexibility factor σ was found to be very high ($\sim$3.0).

In this comparative study, which is part of a systematic investigation on polyacrylic and polymethacrylic esters [2, 3], we have tested different relations expressing the hydrodynamic properties of polymers in solution. The influence of the naphthyl and the corresponding saturated side group on the flexibility of the polymethacrylate chain has been determined.

EXPERIMENTAL

Preparation

Decahydro-β-naphthyl methacrylate (I) was prepared by reaction of methyl methacrylate with decahydro-β-naphthol (mixture of the four isomers) in the presence of p-toluene sulfonic acid [4], and purified by three distillations under reduced pressure (0.5-1 Torr; 96-97°) in the presence of hydroquinone. The purity of the sample was estimated by gas chromatography ($\sim$99.5%).

β-Naphthyl methacrylate (II) was prepared by reaction of methacrylylchloride [5] with β-naphthol in aqueous sodium hydroxide solution [6] and purified by repeated crystallizations from petroleum ether at low temperature to constant melting point (66°).

The two monomers were polymerized at 50° in benzene solution under vacuum with α,α'-bisazoisobutyronitrile. The concentrations of the reagents, in per cent by weight, lay between the following limits:

	Monomer	Initiator
I	20 to 30%	0.02 to 0.07%
II	5 to 20%	0.005 to 0.042%

The polymers were precipitated in methanol, washed with the same solvent, and dried under vacuum.

Fractionation

Ten fractions of polydecahydro-β-naphthyl methacrylate (PDNa) were chosen from among those obtained from five preparations by fractional precipitation at 25° of a 1-2% (w/v) dioxane solution with methanol.

In the case of poly-β-naphthyl methacrylate (PNa), nine fractions were chosen from among those obtained from seven preparations by addition at 25° of isopropanol to a 1-2% (w/v) polymer solution in benzene.

The fractions were dried by the frozen-benzene method. In both cases the range of molecular weight of the fractions was large, extending to around 3×10^6. They were analyzed by gel permeation chromatography at 80° in toluene solution with the Waters G.P.C. 200.

The solvent flow was 1 cc min^{-1}. The calibration was made with the polystyrene (PS) standards, and the method of calculation of Benoît et al. [7] was applied.

The Mark-Houwink relations in toluene at 80° for PS, PDNa, PNa are:

$$[\eta] = 14.77 \times 10^{-5}\, \overline{M}_w^{\,0.69} \quad (\text{PS})$$
$$[\eta] = 7.19 \times 10^{-5}\, \overline{M}_w^{\,0.69} \quad (\text{PDNa})$$
$$[\eta] = 15.56 \times 10^{-5}\, \overline{M}_w^{\,0.58} \quad (\text{PNa})$$

The polydispersity values are given in Table 3.

Microtacticity

The microtacticity of the polymers was determined after hydrolysis with concentrated sulfuric acid and reesterification of the polymethacrylic acid with diazomethane. The NMR spectra were taken at 120° in o-dichlorobenzene with a 100-MHz Varian spectrometer [8].

The following percentages of the triads mm, mr, and rr have been found:

	mm	mr	rr
PDNa	14	37	49
PNa	16	40	44
PMMA	3	32	65

The syndiotactic configuration is consequently less important than in polymethyl methacrylate (PMMA) prepared in similar conditions.

The presence of the aromatic rings decreases slightly the syndiotacticity of the polymer with respect to the corresponding saturated compound.

Intrinsic Viscosity

The viscosities were measured at 25° in a Desreux-Bischoff dilution viscometer [9] with negligible kinetic energy correction. The measurements were carried out in different solvents in the following orders of decreasing intrinsic viscosities of the solutions: benzene, decalin, cyclohexane, and dipropyl ketone for PDNa; tetrahydrofurane (THF), dioxane, and benzene for PNa.

Figures 1 (PDNa) and 2 (PNa) show that, even for the highest molecular weight fractions, the Huggins and Kraemer relations are

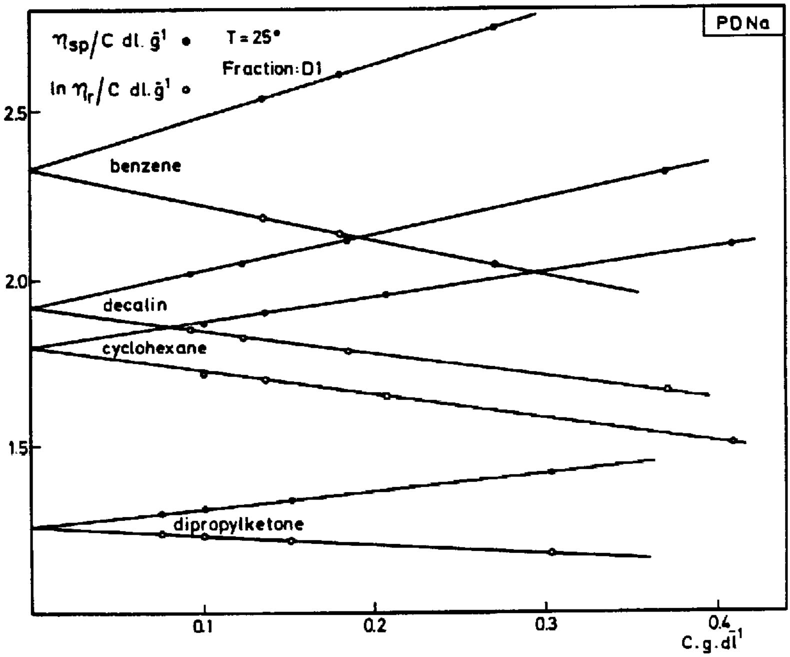

FIG. 1. Viscosity data vs. concentration for Fraction D1 of PDNa in different solvents at 25°.

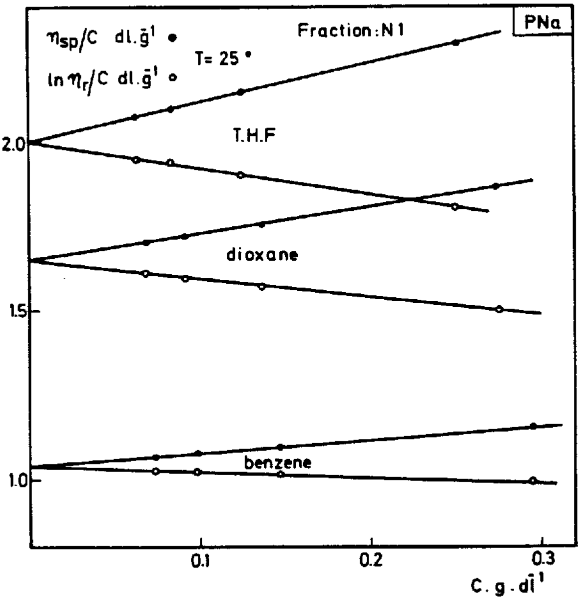

FIG. 2. Viscosity data vs. concentration for Fraction N1 of PNa in different solvents at 25°.

verified in the different solvents. The corresponding values of $[\eta]$ and of the Huggins constant k_h are given in Tables 1 and 2.

The value of k_h for PDNa changes very little with solvent (0.33 for dipropyl ketone, 0.30 for benzene). In the case of PNa the change in the Huggins constant is more important (0.38 for benzene, 0.30 for THF).

Ultracentrifugation

The sedimentation constants were determined at 25° in cyclohexane (PDNa) and benzene (PNa) with a Spinco ultracentrifuge and corrected for the hydrostatic pressure and the dilution by extrapolation to the meniscus [10].

The values of 1/S plotted against the concentration (Figs. 3 and 4) are extrapolated to zero concentration according to the empirical relation [11]:

$$1/S = 1/S_0 (1 + k_s C)$$

TABLE 1. Polydecahydro-β-naphthyl Methacrylate (PDNa)

		Fractions										k_h	k_k
	Solvent	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	Average	value
$[\eta]$ (dl g^{-1})	Benzene	2.33	1.67	1.40	1.13	0.85	0.63	0.53	0.31	0.20	0.16	0.30	0.19
	Decalin	1.92	1.37	1.17	0.94	0.76	0.57	0.46	0.30	0.20	0.16	0.30	0.19
	Cyclohexane	1.80	1.25	1.08	0.85	0.68	0.51	0.43	0.26	0.18	0.14	0.31	0.18
	Dipropylketone	1.26	0.90	0.74	0.63	0.47	0.40	0.28	0.20	0.12	0.11	0.33	0.17
$\overline{M}_w \times 10^{-6}$	Cyclohexane	3.21	1.83	1.42	1.06	0.81	0.48	0.34	0.17	0.10	0.07		
$A_2{}^* \times 10^4$ (cc mole g^{-2})		0.9	0.9	0.9	1.1	1.2	1.1	1.2	0.9	(0.6)	0.8		
$(\overline{r}_z{}^2)^{1/2}$ (Å)		1660	1250	1090	900	780	600	580	360	-	-		
$\overline{M}_n \times 10^{-6}$	Benzene					0.51	0.33	0.26	0.14	0.07			
$A_2 \times 10^4$ (cc mole g^{-2})						1.40	1.48	1.65	1.65	1.73			
$(S_0) \times 10^{15}$	Cyclohexane		47.11	45.09		33.14		25.28		14.48			
k_s			1.74	1.64		1.01		0.67		(0.13)			

TABLE 2. Poly-β-naphthyl Methacrylate (PNa)

		Fractions									k_h	k_k
	Solvent	N1	N2	N3	N4	N5	N6	N7	N8	N9	Average value	
$[\eta]$ (dl g^{-1})	THF	2.00	1.92	1.40	1.19	0.96	0.79	0.53	0.49	0.32	0.30	0.18
	Dioxane	1.65	1.59	1.14	0.99	0.79	0.66	0.46	0.41	0.27	0.34	0.16
	Benzene	1.04	1.00	0.76	0.65	0.52	0.45	0.34	0.31	0.22	0.38	0.14
$\overline{M}_w \times 10^{-6}$	Benzene	2.88	2.76	1.61	1.39	0.91	0.75	0.42	0.36	0.21		
$A_2{}^{*} \times 10^4$ (cc mole g^{-2})		0.2	0.3	0.2	0.3	0.3	0.4	0.2	0.3	0.3		
$(\bar{r}_z{}^2)^{1/2}$ (Å)		1400	1280	990	920	730	700	550	500	--		
$\overline{M}_n \times 10^{-6}$	Benzene					0.66	0.51	0.28	0.25	0.14		
$A_2 \times 10^4$ (cc mole g^{-2})						0.41	0.42	0.42	0.44	0.45		
$(S_0) \times 10^{15}$	Benzene		78.24	57.78		42.68		31.04		23.77		
k_s			1.67	1.04		0.66		0.58		0.38		

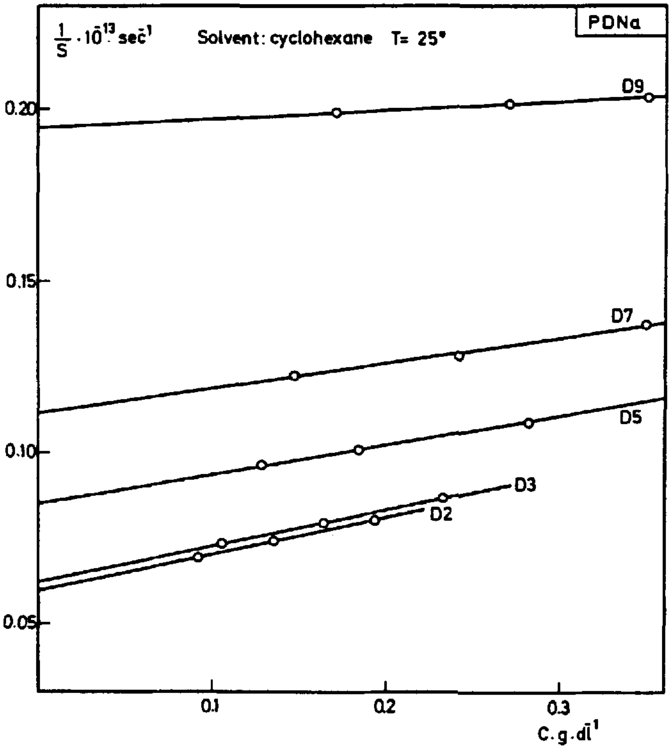

FIG. 3. Sedimentation data vs. concentration for PDNa in cyclohexane at 25°.

The values of k_s of the intrinsic sedimentation constant (S_0) or $(\eta_0/1 - \overline{V}\rho)S_0$ are given in Tables 1 and 2.

The partial specific volume $\overline{V}$, determined by the pycnometric method at 25°, is equal to 0.880 ± 0.001 for PDNa in cyclohexane and to 0.776 ± 0.001 cc g^{-1} for PNa in benzene [reducing factor: 2.82 × 10^{-2} (PDNa) and 1.88 × 10^{-2} (PNa)].

Light Scattering

The experimental data($\overline{M}_w$, A_2^*, $(\overline{r}_z^{\,2})^{1/2}$) given in Tables 1 and 2 were obtained at 25° with a Sofica instrument (5460 Å). The solvents and the solutions were passed through a flotronic membrane.

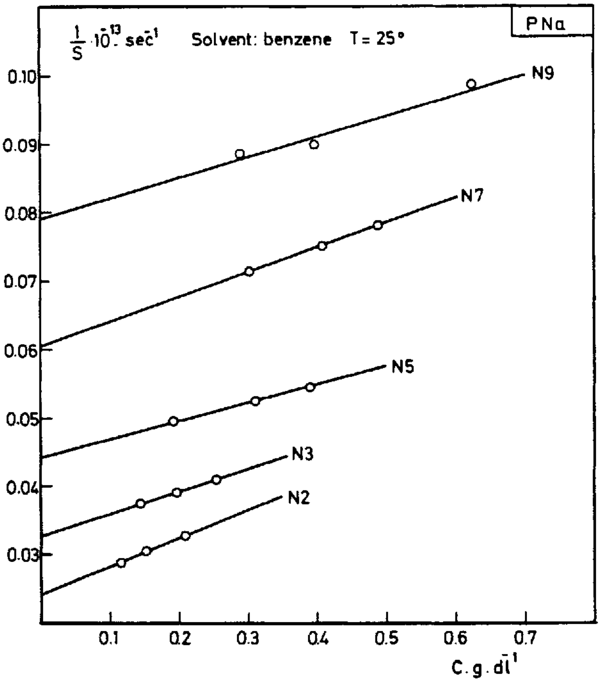

FIG. 4. Sedimentation data vs. concentration for PNa in benzene at 25°.

The refractive index increments under the same conditions are (104 ± 2) × 10^{-3} for PDNa in cyclohexane and (142 ± 2) × 10^{-3} cc g^{-1} for PNa in benzene.

As is often the case, the values of A_2* for the different fractions are not very precise. For PNa in benzene (poor solvent), we find an average value of 0.3 × 10^{-4} cc mole g^{-2}; for PDNa in the good solvent cyclohexane, A_2* is equal to 10^{-4} cc mole g^{-2}.

Osmotic Pressure

The osmotic pressure was determined at 27° with a Knauer electronic osmometer (Sartorius membranes). Benzene solutions were used for both polymers; they were degased before measurement.

The plots of π/C vs C shown in Figs. 5 (PDNa) and 6 (PNa) are

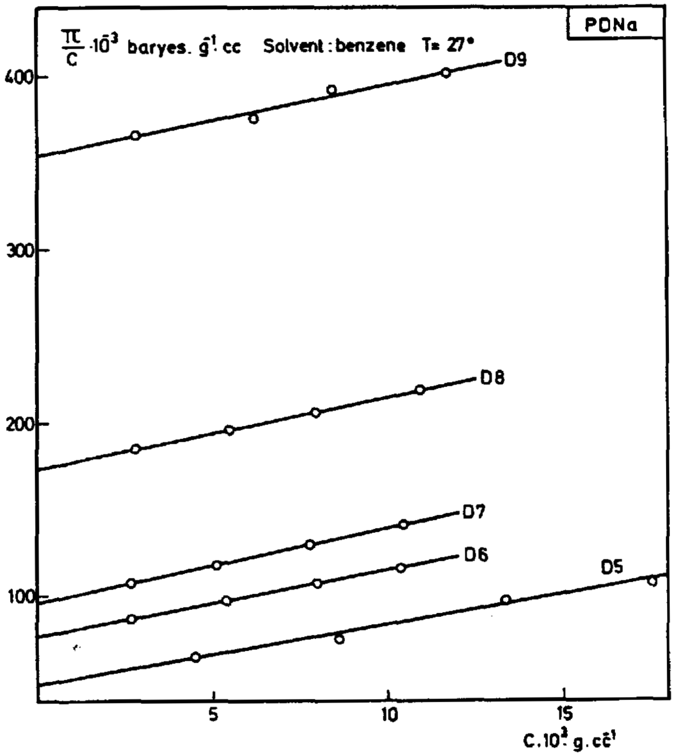

FIG. 5. Osmotic pressure data vs. concentration for PDNa in benzene at 27°.

linear even for the highest molecular weight fraction still measurable.

The values of $\overline{M}_n$ and A_2 are given in Tables 1 and 2.

Polydispersity

The polydispersity factors $\overline{M}_w/\overline{M}_n$ for the different fractions of both polymers are given in Table 3 and are compared with the values found by gel permeation. The agreement is satisfactory.

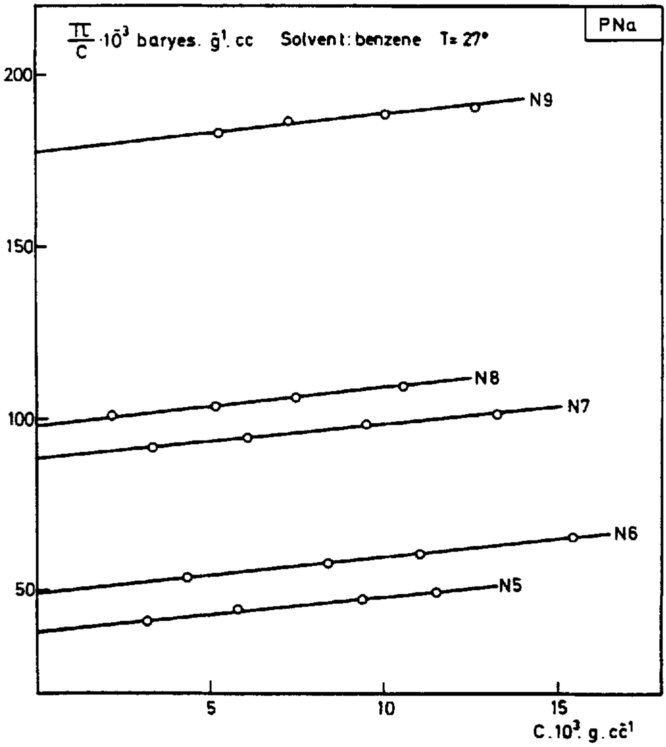

FIG. 6. Osmotic pressure data vs. concentration for PNa in benzene at 27°.

RESULTS AND DISCUSSION

1. The experimental values of the constants for the relations between $[\eta]$ and $\overline{M}_w$ or $\overline{M}_n$ are given in Table 4.

Because the polydispersity of the different fractions are practically identical, the value of the exponent "a" is the same in the two relations.

The other relations are $(S_0) = 10.1 \times 10^{-17} \overline{M}_w^{0.43}$ (PDNa in cyclohexane 25°); $(S_0) = 6.6 \times 10^{-17} \overline{M}_w^{0.48}$ (PNa in benzene 25°).

TABLE 3

PDNa			PNa		
Fraction	$\overline{M}_w/\overline{M}_n$ [a]	GPC $\overline{M}_w/\overline{M}_n$	Fraction	$\overline{M}_w/\overline{M}_n$ [a]	GPC $\overline{M}_w/\overline{M}_n$
D1		1.6	N1		1.8
D2		1.4	N2		1.7
D3		1.4	N3		1.7
D4		1.5	N4		1.8
D5	1.6	1.3	N5	1.4	1.5
D6	1.5	1.5	N6	1.5	1.6
D7	1.3	1.2	N7	1.5	1.6
D8	1.2	1.3	N8	1.4	1.5
D9	1.4	1.6	N9	1.5	1.5
D10		1.4			

[a] Light scattering-osmotic pressure data.

TABLE 4. $[\eta] = K_a \overline{M}_w^{\,a}$, $[\eta] = K_b \overline{M}_n^{\,a}$, 25°

PDNa	Benzene	Decalin	Cyclohexane	Dipropylketone
$K_a \times 10^5$	5.81	6.76	9.22	12.17
$K_b \times 10^5$	7.38	8.52	11.26	13.57
a	0.71	0.69	0.66	0.62
PNa	THF	Dioxane	Benzene	
$K_a \times 10^5$	7.05	10.07	22.84	
$K_b \times 10^5$	9.07	12.84	27.88	
a	0.69	0.65	0.57	

The change of A_2 (osmotic pressure) with the molecular weight is small, especially for PNa in benzene, which is a bad solvent for this polymer. Only the relation for PDNa in a good solvent (benzene at 27°) is significant

$$A_2 = 3.7 \times 10^{-4}\ \overline{M}_n^{\ -0.07}$$

2. As a result of the theory of the equivalent impenetrable sphere [12], a relation exists between S_0, S, $[\eta]$ and C:

$$S = S_0 - kS[\eta]C$$

with k or $k_s/[\eta]$ equal to 1.4-1.6. The experimental values of k for PDNa vary from 1.56 (D7) to 1.40 (D2) and for PNa from 1.73 (N9) to 1.67 (N2), in fair agreement with the expected theoretical value.

3. The values of the constants $\Phi^{1/3}P^{-1}$ of the Mandelkern-Flory equation [13]

$$(S_0)[\eta]^{1/3}M^{-2/3} = \Phi^{1/3}P^{-1}N^{-1}$$

are given in Table 5.

TABLE 5. $\Phi^{1/3}P^{-1} \times 10^{-6}$

	Fraction					Average value
PDNa in cyclohexane	D2	D3	D5	D7	D9	
	2.1	2.2	2.0	2.4	2.3	2.2
PNa in benzene	N2	N3	N5	N7	N9	
	2.4	2.3	2.2	2.2	2.5	2.3

The average value of $\Phi^{1/3}P^{-1}$, with P equal to 5.1, leads to a value of Φ of 1.6×10^{21}, lower than the value corrected for polydispersity or 2.0×10^{21} (PDNa) and 1.9×10^{21} (PNa). We have found the same discrepancy for other polymethacrylates with a bulky substituent [14].

4. The value of K_θ leading to the unperturbed dimension $(\overline{r}_0^{\,2})^{1/2}$

$$K_\theta = \Phi(\overline{r}_0^{\,2}/M)^{3/2}$$

has been calculated in different ways.

a. Stockmayer-Fixman relation [15]:

$$[\eta] M^{-1/2} = K_\theta + 0.51\,\Phi\, B M^{1/2}$$

The plots of $[\eta]\,\overline{M}_w^{-1/2}$ vs $\overline{M}_w^{1/2}$ are given in Fig. 7. The values of K_θ obtained by this relation are 42 × 10^{-5} (PDNa) and 54 × 10^{-5} dl g^{-1} (PNa).

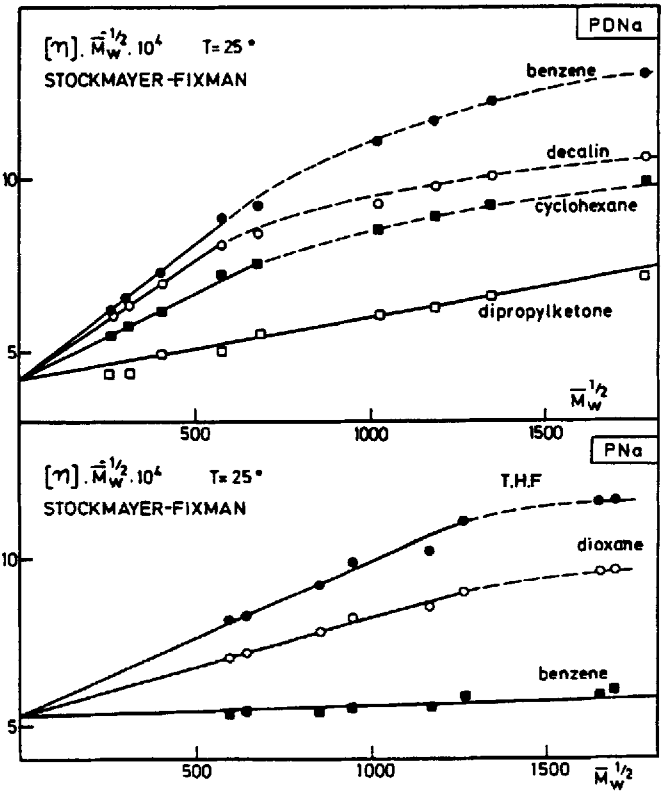

FIG. 7. Stockmayer-Fixman plots for PDNa and PNa in different solvents at 25°.

b. Kurata-Stockmayer relation [16]:

$$[\eta]^{2/3} M^{-1/3} = K_\theta^{2/3} + 0.363\,\Phi\, B g(\alpha) M^{2/3} [\eta]^{-1/3}$$

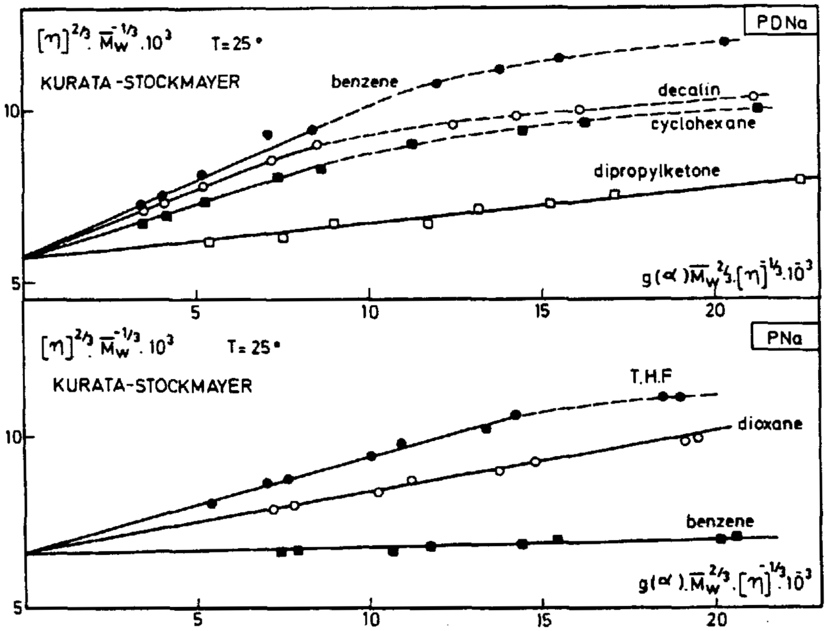

FIG. 8. Kurata-Stockmayer plots for PDNa and PNa in different solvents at 25°.

The plots of $[\eta]^{2/3}\overline{M}_w^{-1/3}$ vs $g(\alpha)\overline{M}_w^{2/3}[\eta]^{-1/3}$ are given in Fig. 8.

The K_θ *values are in excellent agreement with those found from* the Stockmayer-Fixman relation: 43×10^{-5} (PDNa) and 54×10^{-5} dl g^{-1} (PNa).

c. The value of K_θ obtained from the Fox-Flory relation [17]:

$$[\eta]^{2/3}M^{-1/3} = K_\theta^{2/3} + \text{const}\, M[\eta]^{-1}$$

depends on the solvent (Fig. 9); the better the solvent, the lower the value of K_θ. For a hypothetical solvent with zero slope, the extrapolated value agrees with those found above. The same observation has been made for many other polymers [2, 18-20].

As shown in Fig. 9, there is a common point of intersection of all the lines which corresponds to a molecular weight of 4500 (PDNa) and 5000 (PNa). These values agree with the one given by Patel et al. [19].

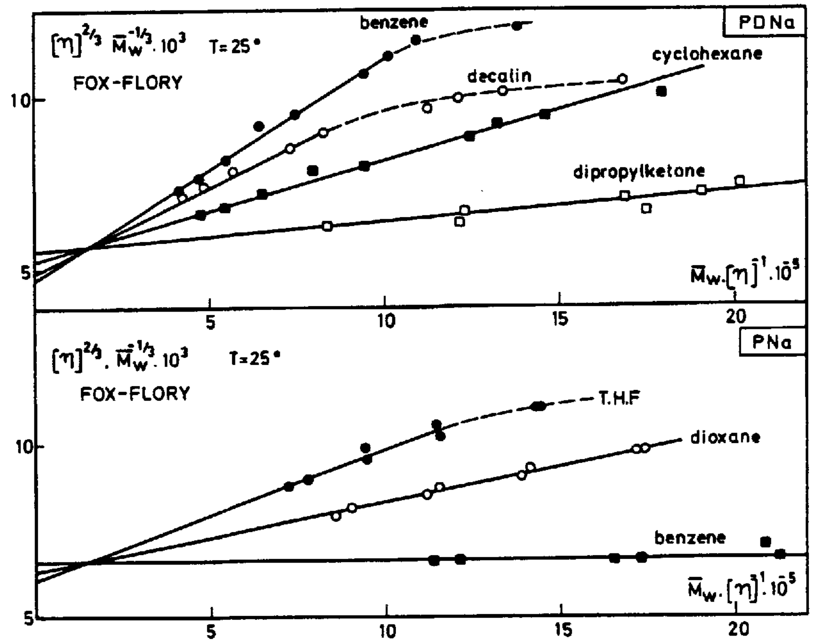

FIG. 9. Fox-Flory plots for PDNa and PNa in different solvents at 25°.

d. The semiempirical relation of Cowie [21]:

$$[\eta]\,M^{-1/2} = \Phi(\epsilon)\,\Phi^{-1}\,K_\theta + 0.9166\,\Phi(\epsilon)\,\Phi^{-1}\,K_\theta K^{7/10} M^{7/20}$$

where $\Phi(\epsilon) = \Phi(1 - 2.63\epsilon + 2.86\epsilon^2)$ and $\epsilon = (2a - 1)/3$, gives K_θ values of the same order for all solvents, or 43×10^{-5} (PDNa) and 53×10^{-5} dl g^{-1} (PNa).

The plots of $[\eta]\overline{M}_w^{-1/2}$ vs $\overline{M}_w^{7/20}$ are given in Fig. 10.

e. Berry's relation [22]:

$$[\eta]^{1/2}\,M^{-1/4} = K_\theta^{1/2} + 0.42\,K_\theta^{1/2}\,\Phi\,BM\,[\eta]^{-1}$$

best fits the experimental data as shown in Fig. 11. The values of K_θ obtained by this relation are 43×10^{-5} (PDNa) and 54×10^{-5} dl g^{-1} (PNa).

f. Figure 12 illustrates the application of the Kamide-Moore relation [23]:

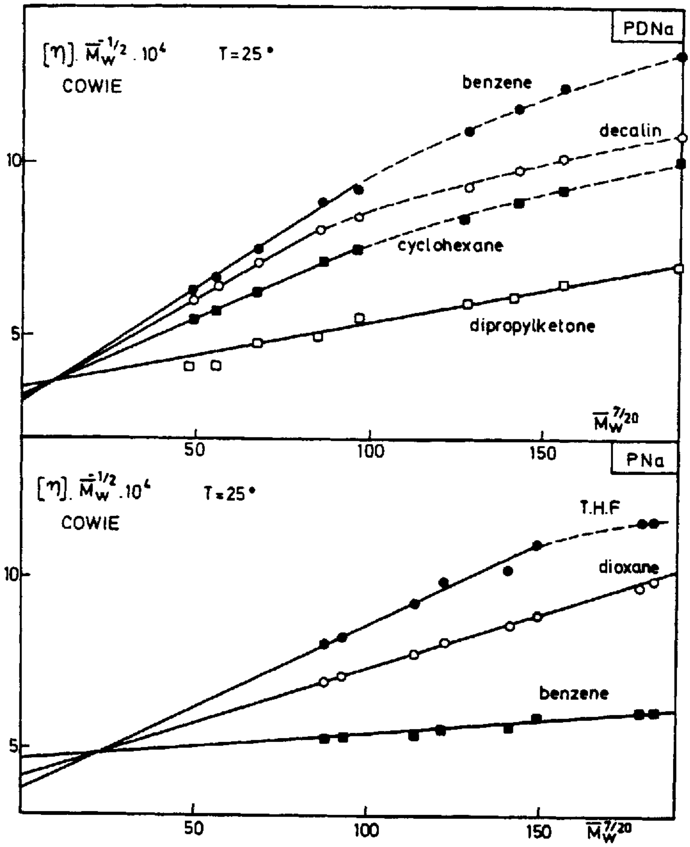

FIG. 10. Cowie plots for PDNa and PNa in different solvents at 25°.

$$-\ln K_a + \ln \left\{ 2\left[(a - 1/2)^{-1} - 2\right]^{-1} + 1 \right\} = (a - 1/2)\ln M_0 - \ln K_\theta$$

using the values of K_a and a of Mark's relation (Table 4) for the different solvents.

The plot of the left-hand side of this equation against (a - 1/2) gives values of K_θ as 41×10^{-5} (PDNa) and 54×10^{-5} dl g^{-1} (PNa).

g. The analysis of the plots of the different relations shows that in the case of PNa, the Stockmayer-Fixman, Kurata-Stockmayer, Cowie

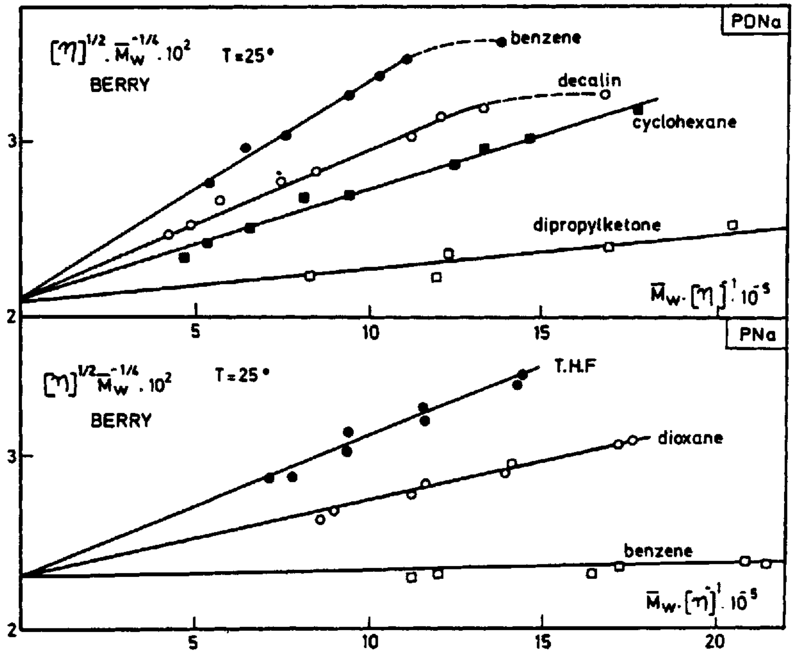

FIG. 11. Berry plots for PDNa and PNa in different solvents at 25°.

and Berry relations are valid practically in the entire molecular weight range and for all the solvents; only at the highest molecular weight and in the very good solvent (THF) is there a slight discrepancy in the case of the three first expressions.

In the case of PDNa these relations are less valid for the high molecular weight fractions in the solvents. The departure from linearity is especially important in the case of the high viscosity solvent decalin.

As mentioned before, the validity of Berry's relation extends to higher molecular weights.

In both cases the Fox-Flory relation is of only limited validity.

h. The calculation of K_θ based on group addivity as suggested by Van Krevelen and Hoftyzer [24] gives values of the same order as those found above.

With M* the molecular weight per main chain atom and S*, a quantity connected with the specific chain stiffness or Σ_i(Si/n), Si being

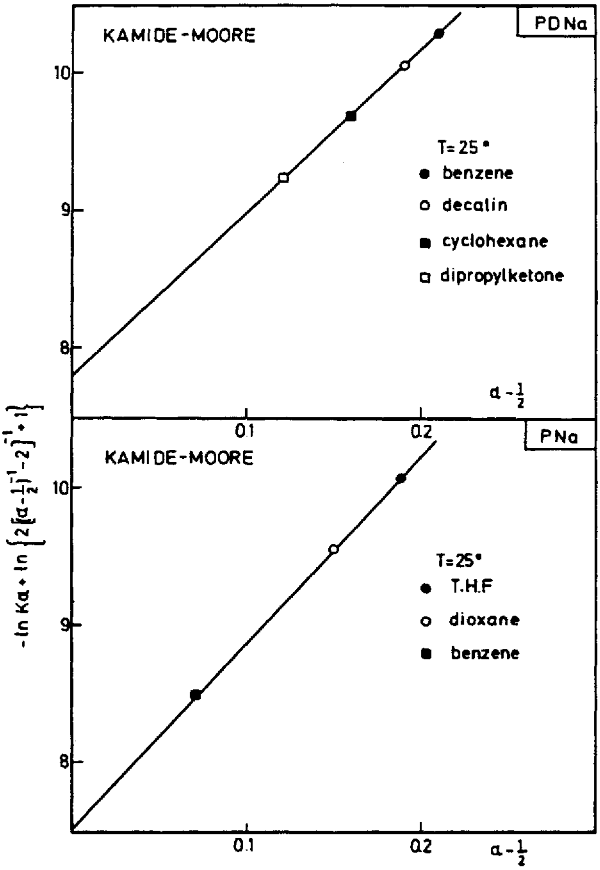

FIG. 12. Kamide-Moore plots for PDNa and PNa at 25°.

the additive constants given by the authors, the calculated values of K_θ or $(S^*/M^{*1/2})^3$ are 44 $\times 10^{-5}$ (PDNa) and 56 $\times$ 10^{-5} dl g^{-1} (PNa).

5. Adopting for K_θ the values of 43 $\times$ 10^{-5} (PDNa) and 54 $\times$ 10^{-5} (PNa), the relations between the root-mean-square end-to-end distance for the unperturbed chain $(\overline{r}_0^2)^{1/2}$ and M are, respectively,

$$(\overline{r}_0^2)^{1/2} = 0.60M^{1/2}\ \text{Å (PDNa)}$$
$$(\overline{r}_0^2)^{1/2} = 0.66M^{1/2}\ \text{Å (PNa)}$$

taking 2.0×10^{21} (PDNa) and 1.9×10^{21} (PNa) for the values of Φ.

The value of $(\overline{r}_0^2)^{1/2}$ always presents an uncertainty due to the assumed value of Φ; consequently this distance for different polymers has only a comparative significance.

6. Figure 13 illustrates the application of the Cowie-Bywater relation based on the sedimentation data [25]:

$$M^{1/2}(S_0)^{-1} = NP\left(\frac{\overline{r}_0^2}{M}\right)^{1/2} + \text{const } M^{1/2}$$

The plot of $M^{1/2}(S_0)^{-1}$ against $M^{1/2}$ gives a value of $(\overline{r}_0^2/M)^{1/2}$ in agreement with those obtained by viscosity.

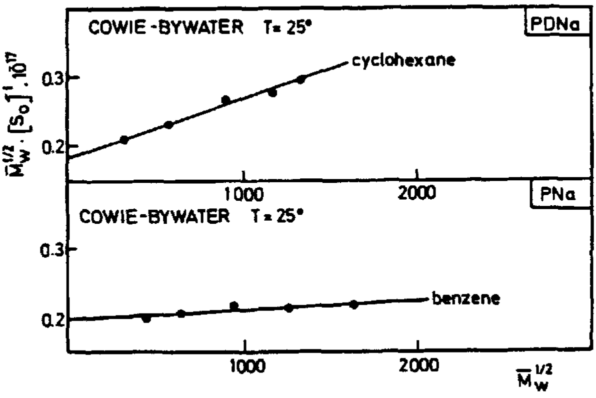

FIG. 13. Cowie-Bywater plots for PDNa and PNa at 25°.

7. The root-mean-square end-to-end distance, assuming completely free rotation around the bonds or $(\overline{r}_{0f}^2)^{1/2}$, is given by practically the same relation for both polymers:

$$(\overline{r}_{0f}^2)^{1/2} = 0.21 M^{1/2}\ \text{Å (PDNa; PNa)}$$

The value $(\overline{r}_{0f}^2)^{1/2}/(\overline{r}_{0f}^2)^{1/2}$ or σ, representing the effect of steric hindrance on the flexibility of the chain, is 2.9 (PDNa) and 3.1 (PNa).

The corresponding expansion factors α, or $(\overline{r}^2)^{1/2}/(\overline{r}_0^2)^{1/2}$, for the lowest and for the highest molecular weight fractions are given in Table 6.

TABLE 6. $\alpha = [\overline{r}^2]^{1/2}/[\overline{r}_0^2]^{1/2}$

Solvent	Benzene	Decalin	Cyclohexane	Dipropyl-ketone	THF	Dioxane
PDNa	1.1-1.4	1.1-1.4	1.1-1.3	1.0-1.2		
PNa	1.0-1.0_5				1.1-1.3	1.0-1.2

This expansion factor increases with the molecular weight for both polymers and in the different solvents. This increase is small in bad solvents and higher in the best solvents.

In Table 7 we summarize the important data characterizing the two polymers. The flexibility factor σ found for PNa is in good agreement with the value obtained by Berdnikova et al. [1] in benzene.

TABLE 7

Characteristics	PDNa	PNa
Microtacticity (rr) (%)	49	44
$K_\theta \times 10^{-5}$ (dl g^{-1})	43	54
$(\overline{r}_0^{\,2})^{1/2}$ (Å)	0.60 $M^{1/2}$	0.66 $M^{1/2}$
$(\overline{r}_{0f}^{\,2})^{1/2}$ (Å)	0.21 $M^{1/2}$	
Flexibility factor σ	2.9	3.1

In conclusion, the two polymers have a very low flexibility as compared to other polymethacrylates with less bulky side groups [26]. However, the fact that PNa has a higher σ value than PDNa definitely shows the specific influence of the aromatic rings on the flexibility of the chain. The same conclusion has been reached in a comparative study of polycyclohexyl and polyphenyl methacrylates [14].

Consequently, it seems that specific interactions between aromatic groups are partly responsible for the high σ value found for PNa. In a study of the microtacticity of various polymethacrylates esters [8], this interaction was also considered to influence the degree of syndiotacticity.

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REFERENCES

[1] K. G. Berdnikova, G. V. Tarasova, V. S. Skazka, N. A. Nikitin and G. V. Dyuzhev, Vysokomol. Soedin., 6, 2057 (1964).

[2] R. Jérome and V. Desreux, Eur. Polym. J., 6, 411 (1970).

[3] M. Tricot and V. Desreux, Makromol. Chem., In Press.

[4] H. J. Barrett and D. E. Strain, British Patent, 468, 890 (1937).

[5] G. H. Stempel, R. P. Cross, and R. P. Mariella, J. Amer. Chem. Soc., 72, 2299 (1950).

[6] S. Patai, Z. Bentov and M. E. Reichmann, J. Amer. Chem. Soc., 74, 845 (1952).

[7] H. Benoît, Z. Grubisic, P. Rempp, D. Decker, and J. G. Zilliox, J. Chim. Phys., 63, 1507 (1966).

[8] J. Niezette and V. Desreux, Makromol. Chem., In Press.

[9] V. Desreux and J. Bischoff, Bull. Soc. Chim. Belg., 59, 93 (1950).

[10] H. G. Elias, Makromol. Chem., 29, 30 (1959).

[11] N. Gralèn, Thesis, Uppsala, 1944.

[12] J. Bischoff, J. Polym. Sci., 17, 81 (1955).

[13] L. Mandelkern and P. J. Flory, J. Chem. Phys., 20, 212 (1952).

[14] N. Hadjichristidis and V. Desreux, To Be Published.

[15] W. Stockmayer and M. J. Fixman, J. Polym. Sci., Part C, 1, 137 (1963).

[16] M. Kurata and W. Stockmayer, Fortsch. Hochpolym. Forsch., 3, 196 (1963).

[17] P. J. Flory and T. G Fox, J. Amer. Chem. Soc., 23, 1904 (1951).

[18] J. Oth and V. Desreux, Bull. Soc. Chim. Belg., 63, 321 (1954).

[19] J. R. Patel, C. K. Patel, and R. D. Patel, Makromol. Chem., 115, 178 (1968).

[20] C. Ceccorulli, M. Pizzoli, and C. Stea, Makromol. Chem., 142, 153 (1971).

[21] J. M. G. Cowie, Polymer, 7, 487 (1966).

[22] G. C. Berry, J. Chem. Phys., 46, 1338 (1967).

[23] K. Kamide and W. R. Moore, J. Polym. Sci., Part B, 2, 809 (1964).
[24] D. W. Van Krevelen and P. J. Hoftyzer, Rubber Chem. Tech., 42, 462 (1969).
[25] J. M. G. Cowie and S. Bywater, Polymer, 6, 197 (1965).
[26] S. N. Chinai et al., J. Polym. Sci., 17, 391 (1955); 19, 463 (1956); 21, 417 (1956); 25, 413 (1957); 33, 471 (1958); 43, 557 (1960).

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