

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Dilute Solution Properties and Conformation of Polyacenaphthylene

J. Moacanin^a; A. Rembaum^a; R. K. Laudenslager^a; R. Adler^a

^a JET PROPULSION LABORATORY CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA

To cite this Article Moacanin, J. , Rembaum, A. , Laudenslager, R. K. and Adler, R.(1967) 'Dilute Solution Properties and Conformation of Polyacenaphthylene', Journal of Macromolecular Science, Part A, 1: 8, 1497 — 1518

To link to this Article: DOI: 10.1080/10601326708053788

URL: <http://dx.doi.org/10.1080/10601326708053788>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Dilute Solution Properties and Conformation of Polyacenaphthylene*

J. MOACANIN, A. REMBAUM, R. K. LAUDENSLAGER,
and R. ADLER

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

Summary

Several polymerization techniques were investigated to obtain high molecular weight polyacenaphthylene. Thermal polymerization was found to yield molecular weights of over 2,000,000.

A number of polyacenaphthylene fractions were characterized by means of light scattering, osmotic pressure, and viscosity determinations in a theta solvent and in benzene. The following intrinsic viscosity, molecular weight relationships were established:

$$\begin{aligned} [\eta] &= 0.72 \times 10^{-4} \times M_w^{0.72} && \text{in benzene at } 25^\circ \\ [\eta] &= 4.56 \times 10^{-4} \times M_w^{0.50} && \text{in 1,2-dichloroethane at } 35^\circ\text{C} \end{aligned}$$

Although considerable hindrance to rotational motion of chain segments should be expected, the solution behavior could be interpreted in terms of current two-parameter theories for flexible chains. The theta dimensions determined by light scattering were in agreement with those estimated from intrinsic viscosity, and were found to be comparable to those for polystyrene. Also, application of first-order perturbation theory to second virial coefficient data yielded reasonable estimates of the radius of gyration. The high degree of internal consistency among the various measurements rules out the occurrence to any significant extent of branching reactions during thermal polymerization.

Examination of molecular models indicates that threodiisotactic is by far the most probable of the four possible stereoconfigurations. Thus steric considerations along with crystallinity which was observed in all samples suggest considerable stereoregularity.

* This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.

TABLE 1
Anionic Polymerization of Acenaphthylene (9)

Sample	Initiator	Initiator concn., wt. %	Temp., °C	Time, hr	Yield, %	Yield after reprecipitation, %	M_w
AC-1 ^a	Na	Excess	25	3.5	8.0	—	—
AC-2	Na	1.0	25	3.5	1.0	—	—
AC-3	Li	0.3	25	3.5	17.6	—	—
AC-4	Li	0.7	25	3.5	23.2	15.0	2,500
AC-9	Li	9.7	25	3.5	80.4	57.2	2,500
AC-10	Li	0.7	25	21.0	84.3	75.7	—
SPA-2 ^a	Li	0.7	95	21.0	96.0	88.0	14,500

^a Carried out in high vacuum.

Low molecular weight polymers of acenaphthylene were first obtained about 40 years ago (1). Few studies of this system have been described since that time (2-4), and scanty information is available on the fundamental nature and mechanism of the polymerization process. Our investigations of the anionic polymerization of acenaphthylene (Table 1) showed that this monomer may be reacted with alkali metals at room temperature to give a good yield of low molecular weight polymer, but by means of free-radical techniques we were able to synthesize polyacenaphthylene (PACN) of weight-average molecular weight (M_w) over 500,000 and isolate fractions of M_w as high as 3,000,000.

The earliest published studies on dilute solution properties are by Mohorcic and Vene (5,6), who investigated the viscosity and light scattering behavior in tetrahydrofuran solution. Our preliminary results included molecular weight-intrinsic viscosity correlations in benzene and a theta solvent (7). During the preparation of this manuscript a paper by Springer et al. (8) appeared which confirmed our results on solution properties in benzene. During the present investigations PACN fractions were characterized by means of light scattering, osmotic pressure, and viscosity determinations in a theta solvent and in benzene. The results of the dilute solution studies show that the theta radius of gyration for PACN is comparable to that for polystyrene of equal degree of polymerization. Calculations show, however, that free rotation dimensions for the threo and erythro, the two possible PACN isomers, differ by

a factor of two. However, since direct information on stereosequences in the chain is not available, a quantitative analysis of the chain conformation could not be carried out. But examination of molecular models indicates that because of steric considerations the threo configuration is more likely. Also, the observation of crystalline X-ray patterns for the polymer suggests a considerable degree of stereoregularity.

FREE-RADICAL POLYMERIZATION

All polymerization runs described below were carried out in sealed flasks and under high vacuum. A summary of the results obtained by benzoyl peroxide initiation and bulk polymerization is shown in Table 2.

The polymers were obtained as white to pale-yellow powders by precipitation from methanol. An analysis of the results presented in Table 2 leads to the following conclusions:

1. Higher conversions are obtained at higher temperatures, longer reaction times, and in the presence of peroxides.
2. Bulk polymerization yields the same amount of polymer with

TABLE 2
Free-Radical Polymerization of Acenaphthylene

Sample	Time, hr	Temp., °C	Solvent	Initiator concn., wt. % $\times 10^{-2}$	Yield, %	Yield after reprecipitation, %	M_w
BPA-1	72	100	—	—	37.0	—	—
BPA-2	72	150	—	—	83.3	—	—
BPA-3	72	125	—	—	79.5	—	—
BPA-4	24	100	—	2.5	67.5	66.2	285,000
BPA-5	24	125	—	2.5	74.3	73.5	335,000
BPA-6	24	150	—	2.5	86.0	83.0	180,000
SPA-1	24	100	THF	2.5	46.0	42.8	160,000
SPA-4	24	100	THF	—	9.6	—	—
BPA-7	24	100	—	—	15.1	—	—
BPA-8	24	100	—	2.5	66.6	—	—
BPA-9	24	125	—	—	71.5	—	—
BPA-10	24	150	—	—	85.5	—	215,000
BPA-11	72	100	—	2.5	68.0	—	—
JN-5	120	125	—	—	72.7	—	820,000

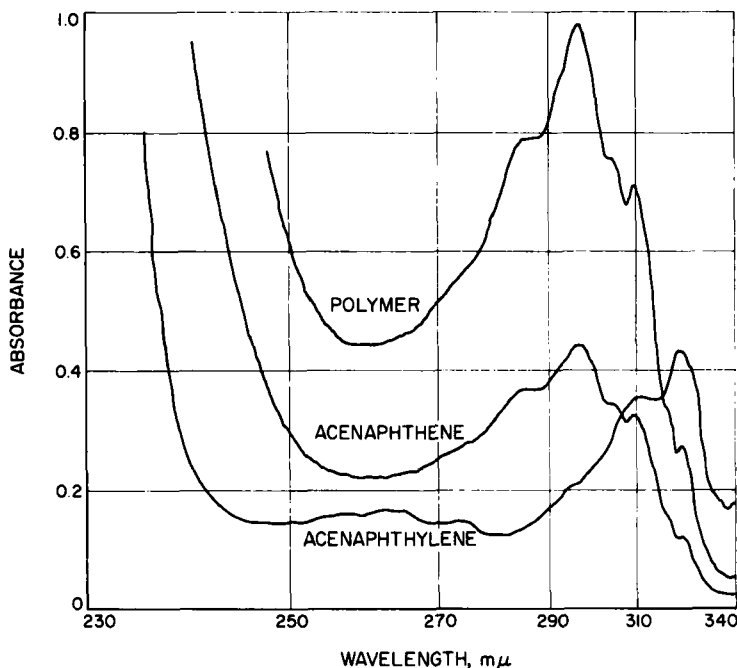


FIG. 1. Ultraviolet spectra of polymer, acenaphthylene, and acenaphthene.

or without the peroxide initiator at 150°C; however, at lower temperature, 100°C, the yield is considerably enhanced by means of benzoyl peroxide initiation.

3. The loss of polymer on precipitation is of the order of 4% in the case of free radical and 16% in the case of Li-initiated polymerization. The molecular weights are distinctly different for the two types of polymerization.

SPECTROPHOTOMETRIC RESULTS

The UV spectra of polymers prepared by alkali metal initiation were practically identical with those obtained by bulk or benzoyl peroxide-initiated polymerization. The same does not hold true, however, for the IR spectra.

In Fig. 1 are shown the UV spectra of the polymer together with those of acenaphthylene and acenaphthene. In Table 3 their extinction coefficients are recorded at 296, 309, and 322 mμ.

In Fig. 2, the IR spectra of the polymer (BPA-11) and of the mono-

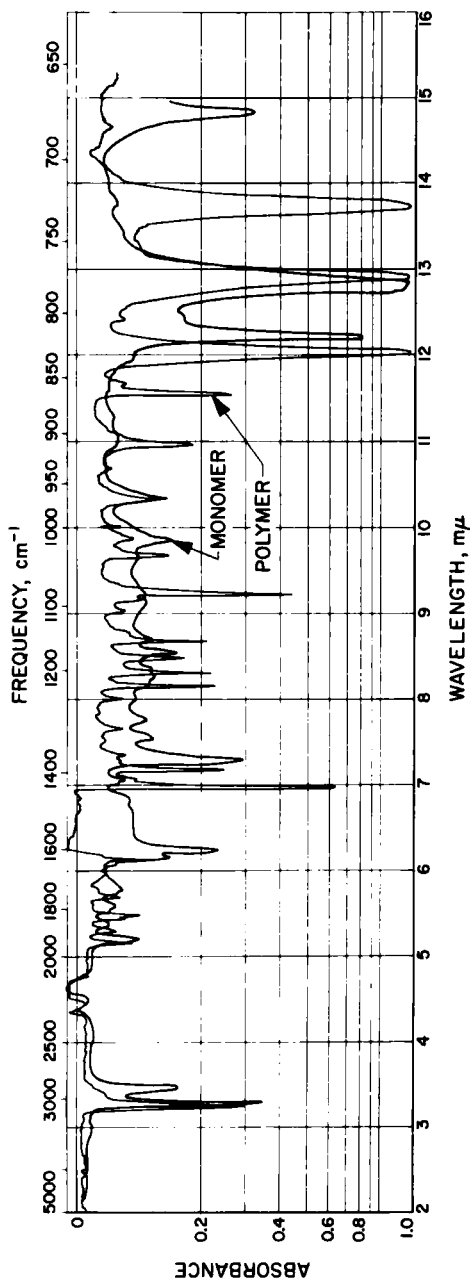


FIG. 2. Infrared spectra of acenaphthylene and benzoyl peroxide-initiated polymer, BPA-11 (Table 2).

TABLE 3
Extinction Coefficients of Poly- and Monoacenaphthylene

Sample	Extinction coefficients, $l\ g^{-1}/cm$, at		
	296 $m\mu$	309 $m\mu$	322 $m\mu$
AC-9	42.8	30.6	—
BPA-11	44.8	—	10.5
BPA-11/F1	37.3	—	8.0
BPA-11/F12	37.6	—	8.1
Acenaphthylene	—	54.6	71.8

mer are compared. PACN prepared by anionic polymerization exhibited IR absorption peaks at 12.7, 13.1, and 14.7 μ not found in the peroxide-initiated polymers. Changes in aromatic substitution are normally observed in this as well as in the 5–6 μ wavelength range. Considering, however, that in the region between 5 and 6 μ both polymers (i.e., those prepared by Li and benzoyl peroxide initiation) are found to have an identical absorption and also in view of the fact that the UV absorption spectrum is the same for both types of polymers, one may conclude that in the polyacenaphthylene prepared by Li initiation, the extra absorption peaks in the IR spectrum must be due to polymerization by-products, in agreement with previous results (2–4). The same reason may ac-

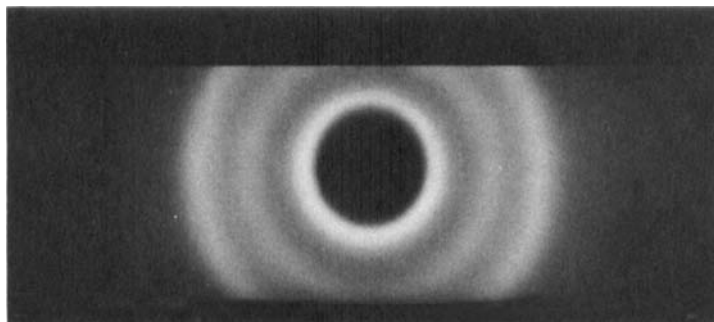


FIG. 3. X-ray diffraction pattern for BPA-5 (Table 2).

count for the fact that the UV absorption spectrum of the polymer differs from that of acenaphthene.

X-RAYS

Powder X-ray patterns were obtained on a number of fractions purified by reprecipitation. All samples exhibited a crystalline pattern and a typical result is shown in Fig. 3. The presence of crystallinity does not appear to depend on polymerization conditions. It seems surprising therefore that polymerization of acenaphthylene in the solid state was reported to yield amorphous polymers (10).

SOLUTION PROPERTIES

Experimental

Fractions for the study were obtained by fractional precipitation from benzene using methanol as the precipitant. The following fractions from preparations obtained by free-radical polymerization in solution were used: FR-I fractions were obtained from polymer BPA-11 (Table 2); FR-II fractions were obtained from polymer BPA-5 (Table 2). The preparation JN-5 obtained by thermal polymerization in bulk was separated into four fractions, and the first fraction was then refractionated into four fractions designated FR-IV.

For the study of solution properties benzene and toluene were used as solvents. The theta solvent was 1,2-dichloroethane at 35°C. The first series of measurements were carried out at 30°C, but light-scattering plots exhibited a slightly negative slope. The 5°C change in temperature, however, did not markedly affect $[\eta]$.

Light-scattering measurements were made with a Brice-Phoenix photometer. Refractive index increments, dn/dc , determined with a Brice-Phoenix differential refractometer, were observed to be as follows: in benzene at 25°C, 0.225 for 436 $m\mu$ and 0.119 for 546 $m\mu$; in 1,2-dichloroethane at 35°C, 0.264 for 436 $m\mu$ and 0.238 for 546 $m\mu$.

Osmotic-pressure measurements on FR-I fractions were carried out at 30°C in toluene using static osmometers with No. 600 cellophane membranes (Stabin, Inc., New York). Some diffusion through

TABLE 4
Partial Specific Volumes at 25°C

Polymer	Solvent	v_1 , ml/g	V_1 , ml/mole monomer
Polystyrene	Benzene	0.92	93
Poly(4-vinylbiphenyl)	DME	0.82	148
Polyacenaphthylene	Benzene	0.77	117
Poly(1-vinylnaphthalene)	Toluene	0.82	126
Poly(2-vinylnaphthalene)	Toluene	0.84	134

the membranes of low molecular weight species was observed. For FR-II fractions, osmotic pressure determinations were made in toluene solutions at 37°C using a Mechrolab High-Speed Osmometer, Model 501 (Mechrolab Inc., Mountainview, California). No drift was observed during these measurements, which take only a few minutes as compared to 2 or 3 days for those with the static osmometers. The drift observed with the latter was doubtless caused by the slow degradation of the polymers in solution (see below).

Solution viscosities were determined with Cannon-Ubbelohde suspended level dilution viscometers. The kinetic energy correction was negligible; solvent efflux times were 230 to 370 seconds.

TABLE 5
Light-Scattering and Viscosity Data on FR-I Fractions in Benzene at 25°C

Fraction	Cumulative wt. %	$M \times 10^{-3}$	$A_2 \times 10^4$	$[\eta]$, dl/g	k_1
1	100	607	0.98	0.73	0.50
2	91.3	781	0.98	0.64	0.46
3	85.1	500	1.03	0.50	0.46
4	75.5	—	—	—	—
5	66.7	—	—	—	—
6	62.6	272	1.00	0.35	0.51
7	54.1	—	—	—	—
8	49.0	—	—	0.28	0.57
9	43.0	147	1.21	0.22	0.61
10	36.2	—	—	—	—
11	32.2	—	—	0.17	0.57
12	26.2	73	1.36	0.13	0.69

TABLE 6
Viscosity Data on FR-II Fractions

Fraction	Cumulative wt. %	1,2-Dichloroethane at 30°C		Benzene at 25°C		Toluene at 25°C	
		$[\eta]$, dl/g	k_1	$[\eta]$, dl/g	k_1	$[\eta]$, dl/g	k_1
(Unfractionated polymer)		—	—	0.27	0.56	0.39	0.65
1	97.5	0.31	0.70	0.47	0.66	0.39	0.65
2	80.8						
3	73.8	0.24	0.69	0.35	0.56	0.31	0.58
4	67.3						
5	59.3	0.19	0.69	0.26	0.49		
6	52.3						
7	45.6	0.18	0.73	0.23	0.62		
8	40.8						
9	34.9	0.15	1.02	0.20	0.36		
10	29.7						
11	27.0					0.13	0.66
12	22.8	0.07	1.33	0.09	0.78		

Partial specific volumes in benzene were determined from density measurements on polymer solutions and were accurate to ± 0.005 ml/g. The results along with data on some vinylaromatic polymers are given in Table 4.

Results

Results on fractions FR-I are summarized in Table 5 along with light-scattering and viscosity data in benzene at 25°C. Results on fractions FR-II are summarized in Table 6 along with viscosity data in benzene and toluene, both at 25°, and 1,2-dichloroethane at 30°C; light-scattering results are given in Table 7. Results on fractions FR-IV are given in Table 8; for these M_w and radii of gyration were obtained from Zimm plots.

A double logarithmic plot of $[\eta]$ vs. M_w for benzene solutions at 25°C is shown in Fig. 4. For the theta solvent the plot of $[\eta]$ vs. $M^{1/2}$ was found to be linear (Fig. 5), in agreement with theory. The

TABLE 7
Molecular Weights and Second Virial Coefficients for FR-II Fractions

Fraction	Benzene at 25°C		1,2-Dichloroethane at $\theta = 30^\circ\text{C}$		Toluene at 30°C	
	$M_w \times 10^{-3}$	$A_2 \times 10^4$	$M_w \times 10^{-3}$	$A_2 \times 10^4$	$M_n \times 10^{-3}$	$A_2 \times 10^4$
(Unfractionated polymer) ^a	174	0.46	149	0.00	56	0.44
1	403	1.10	407	0.00	250	1.21
2	—	—	—	—	216	1.37
3	269	1.21	254	0.00	181	1.61
5	195	0.99	190	0.00	—	—
7	126	1.52	—	—	—	—
9	94	1.55	101	0.00	—	—
11	—	—	—	—	54	2.01
12	36	2.01	—	—	—	—

^a Polymer BPA-5, Table 2.

Mark-Houwink parameters are listed in Table 9 along with literature results on polystyrene, poly(α -methylstyrene), and poly(2-vinylnaphthalene).

It was observed that PACN solutions undergo slow degradation on standing. Gradual changes in viscosity took place over a 1-week period even when the experiment was carried out in an evacuated

TABLE 8
Solution Properties Data for FR-IV

Fraction	Viscosities				Light scattering in theta solvent		Osmotic pressure in theta solvent
	Benzene (25°C)		Theta sol- vent (35°C)		M_w	$(\bar{h}_z^2)^{1/2}, \text{Å}$	M_n
	$[\eta]$	k_1	$[\eta]_\theta$	k_1			
F1	1.50	0.39	0.53	0.59	2,310,000	930	1,870,000
F2	1.10	0.43	0.52	1.08	1,220,000	780	1,140,000
F3	0.71	0.41	0.38	0.59	650,000	560	380,000
F4	0.37	0.28	—	—	—	—	—

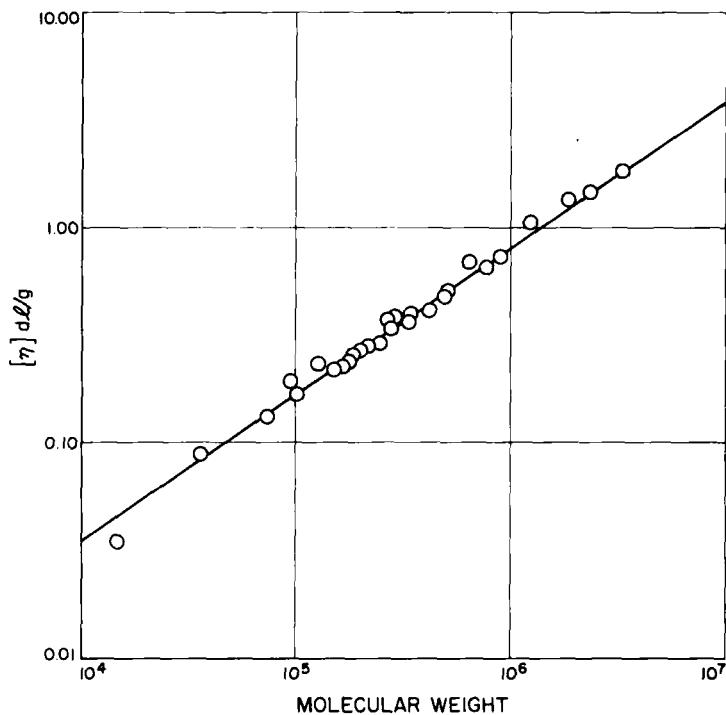


FIG. 4. Log $[\eta]$ vs. log M_w plot for benzene solution at 25°C.

TABLE 9

Mark-Houwink Parameters for PAcN and Some Vinylaromatic Polymers

Polymer	Solvent	Temp., °C	k_1 $\times 10^4$	a	$\left(\frac{\bar{r}_g^2}{\bar{r}_{g,PS}^2}\right)^{1/2}$	Ref.
Polystyrene	Cyclohexane	34	8.20	0.50	1.00	24
Poly(α -methylstyrene)	Cyclohexane	38	7.50	0.50	1.02	24
Poly(4-vinylbiphenyl)	DME	25	3.70	0.53		7
Poly(4-vinylbiphenyl)	Benzene	25	0.92	0.69		7
Poly(4-vinylbiphenyl)	2-Methoxyethanol/ dimethoxyethane	30	4.40	0.50	1.10	7
PAcN	Benzene	25	0.72	0.67		7
PAcN	1,2-Dichloroethane	30	4.56	0.50	1.04	7
PAcN	Tetrahydrofurane	20	9.66	0.87		6
Poly(2-vinyl- naphthalene)	Benzene	20	0.66	0.71		25
	Decalin/toluene	30.2	5.20	0.50	1.05	25

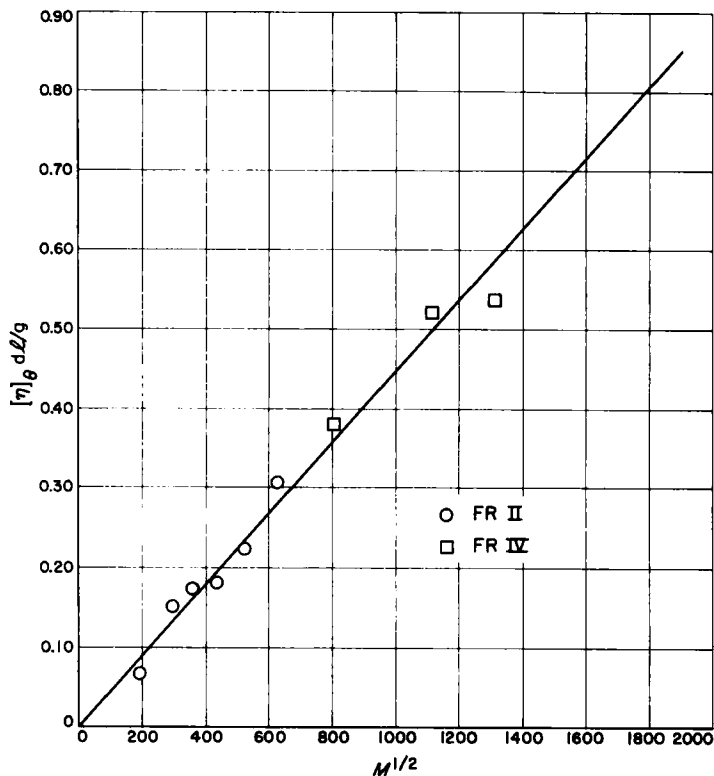


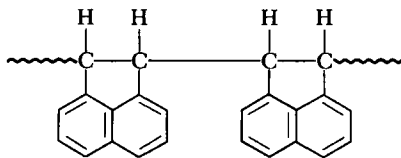
FIG. 5. $[\eta]_0$ vs. $M_w^{1/2}$.

sealed viscometer to eliminate the possible effect of air. The degradation of polyacenaphthylene in solution was investigated in more detail by Utracki et al. (11). The mechanism of degradation is not understood, but appears to be promoted by absorption of light (12).

For each experiment, solutions were freshly prepared and measurements carried out within 24 hr. Although following this procedure and working in dilute solutions (11) the effect of degradation on the results was minimized, the possibility of some additional scatter in correlations of results from different measurements cannot be discounted.

DISCUSSION

In PACn every other backbone C—C bond is part of the cyclic repeating unit:



Therefore, in contrast to polystyrene or other vinylaromatic polymers, only one-half of the backbone bonds can rotate. This structural feature, along with the bulkiness of the substituent, should impart considerable stiffness to the polymer chain and lead to an expanded coil conformation in solution. The high glass transition temperature, $T_g = 260^\circ\text{C}$ (13), for this polymer, as compared to 100°C for polystyrene, is an expected consequence of greatly hindered bond rotation (14). Another feature is that in each repeating unit both carbons are asymmetric, which leads to four possible stereoconfigurations: threo and erythro, each configuration being either diiso- or disyndiotactic (15). The importance of this feature to conformation is discussed below.

Turning our attention to the question of stiffness, it is surprising to find that in dilute solution this polymer appears to behave in a manner expected for flexible chains. Thus Fig. 4 shows that the Mark-Houwink relationship is obeyed over a wide molecular weight range with an exponent in benzene of 0.67; also, the theta intrinsic viscosity is proportional to $M^{1/2}$ (Fig. 5).

To further test for the internal consistency of the data we use the

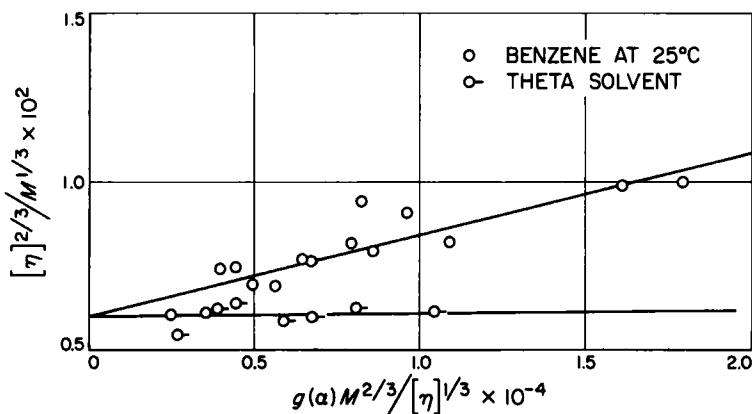


FIG. 6. Viscosity plot according to Eq. (1).

following equation from the Kurata-Stockmayer-Roig theory (16):

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + 0.363\phi_0 B [g(\alpha_\eta) M^{2/3}/[\eta]^{1/3}] \quad (1)$$

where

$$\begin{aligned} K^{2/3} &= \phi^{2/3} \langle L^2 \rangle / M \\ B &= 2V_1 (\frac{1}{2} - \chi) / c^2 m^2 \\ g(\alpha_\eta) &= 8\alpha_\eta^3 / (3\alpha_\eta^2 + 1)^{3/2} \\ \alpha_\eta^2 &= [\eta] / [\eta]_0 \end{aligned}$$

χ is Flory's interaction parameter, V_1 the solvent molecular volume, c the chain constant of the order of unity, and m the molecular weight. Plots of the above function are reasonably linear for both benzene and 1,2-dichloroethane solutions (Fig. 6). The common intercept for the two solvents of about 0.58 yields $K = 4.6 \times 10^{-4}$, in agreement with 4.56×10^{-4} given by the slope of the $[\eta]_0$ vs. $M^{1/2}$ plot (Table 9). Data from Vene and Mohorcic (6) for solutions in THF at 20°C also give a linear plot, but with an intercept at about 0.72. The reason for this discrepancy is not understood, but it may be caused in part by differences in polydispersity between the fractions of these authors and ours; they find experimentally that $\phi = 2.0 \times 10^{21}$, as compared to our value of 1.4×10^{21} (see below).

The slope of the benzene straight line gives $B = 0.25 \times 10^{-7}$ (Fig. 6) as compared to 1.05×10^{-7} for polystyrene in toluene. With appropriate numerical substitutions, and assuming c to have the same value for both polymers, the results offer the following comparison:

$$(\frac{1}{2} - \chi_{\text{PAcN}}) = (0.63)(\frac{1}{2} - \chi_{\text{PS}})$$

Taking $\chi_{\text{PS}} = 0.44$ (17), we get $\chi_{\text{PAcN}} = 0.46$, a value which seems to be reasonable and is also consistent with the slightly lower Mark-Houwink exponent for PAcN: 0.67 vs. 0.70 for PS.

Although originally assumed constant, the Huggins parameter k_1 was shown recently to be a slowly varying function of molecular weight (18,19). This is confirmed for PAcN by the plot of k_1 vs. M shown in Fig. 7. There is a definite increase in k_1 as M is decreased below 100,000. The same trend was observed with polystyrene, but the significant change occurred at somewhat lower molecular weights ($\approx 50,000$). This may not be surprising, since the monomer

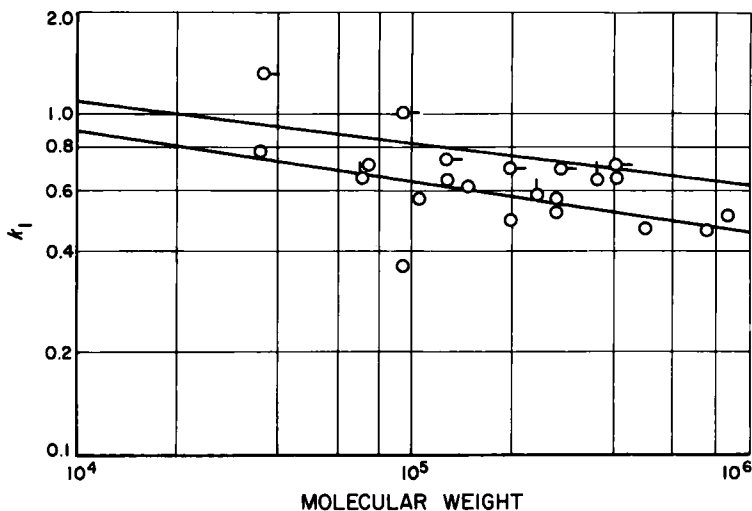


FIG. 7. Huggins' parameter k_1 vs. molecular weight.

molecular weight for PS is about two-thirds that of PAcN (104 vs. 152).

To discuss the unperturbed dimensions obtained from Zimm's plots, we use Flory's relationship (see, for example, Ref. 16):

$$[\eta]_{\theta} = KM^{1/2} = \phi \frac{(\bar{h}_0^2)^{3/2}}{M} \equiv \phi (\bar{h}_0^2/M)^{3/2} M^{1/2} \quad (2)$$

where K is the Mark-Houwink empirical constant, ϕ Flory's nearly universal parameter, and \bar{h}_0^2 the unperturbed mean-square end-to-end distance. For a given polymer $(\bar{h}_0^2/M)^{1/2}$ should be a constant, independent of molecular weight. The values for this ratio given in Table 10 were calculated from \bar{h}_0^2 and M_w data, both obtained from light-scattering measurements. Reasonable agreement is observed for the three fractions. Using these data along with $[\eta]_{\theta}$

TABLE 10

Poly(acenaphthylene) Parameters Corrected for Heterogeneity

Fraction	M_w/M_n	$M_z/M_w = \frac{k+2}{k+1}$	$[(\bar{h}_0^2)_z/M_w]^{1/2}$ $\times 10^{11}$	ϕ_z $\times 10^{-21}$	$\phi_0 \approx \phi_z (M_z/M_w)^{3/2}$ $\times 10^{-21}$	$[(\bar{h}_0^2)_z/M_z]^{1/2}$ $\times 10^{11}$
IV-F1	1.24	1.2	610	1.54	2.02	560
IV-F2	1.04	1.04	710	1.34	1.42	690
IV-F3	1.70	1.4	690	1.43	2.38	580

and Eq. (2), we obtain for ϕ about 1.4×10^{21} (Table 10), a value which is considerably lower than the $2.1\text{--}2.8 \times 10^{21}$ range usually observed for linear polymers. However, the effect of polymer heterogeneity on this value has to be estimated because the experiments yield weight averages for $[\eta]$ and M , and a z average for \bar{h}_θ^2 .

A reasonable estimate of the correct value of ϕ can be made using the Schulz exponential distribution, which yields the following relationships for the weight and z averages for ϕ (16):

$$\begin{aligned} \phi_w &= q_w \phi & q_w &= \Gamma(k + 1.5) / [(k + 1)^{1/2} \Gamma(k + 1)] \\ \phi_z &= q_z \phi & q_z &= [(k + 1) / (k + 2)]^{3/2} q_w \end{aligned} \quad (3)$$

where Γ represents the gamma function and the heterogeneity parameter k is calculated from experimental M_n and M_w along with

$$k/M_n = (k + 1)/M_w = (k + 2)/M_z \quad (4)$$

Deviations from unity for q_w can be neglected, since they usually are well within experimental uncertainties; e.g., $q_w = 0.94$ for $M_w/M_n = 2$. Hence in practice it is sufficient to consider only the factor $[(k + 1)/(k + 2)]^{3/2}$. Data corrected for heterogeneity following this procedure are included in Table 10.

The corrected ϕ for fractions 1 and 3 are within the expected range. The relatively large uncertainty in osmotic-pressure measurements on high molecular weight polymers may account for the low value for fraction 2; its ϕ could be brought in the normal range with $M_w/M_n \approx 1.3$, a more reasonable value than the exceptionally low observed value.

Giving more weight to fractions 1 and 3, the reduced root-mean-square end-to-end distance $[(\bar{h}_\theta^2)_z/M_z]^{1/2}$ is about 600×10^{-11} a value to be compared with 670×10^{-11} for polystyrene (PS). For an equal degree of polymerization we have

$$(\bar{h}_{\theta, \text{PACN}}^2 / \bar{h}_{\theta, \text{PS}}^2)^{1/2} = (M_{\text{AcN}}/M_{\text{S}})^{1/2} (600/670) = 1.08$$

in reasonable agreement with 1.04, estimated from theta viscosity measurements (Table 9).

To calculate the dimensions of PACN we followed a procedure described by Volkenstein (20) to derive an expression for the mean-square end-to-end distance \bar{h}^2 . The model for the chain consists of two alternating bonds, the rotational potentials for one bond being characterized by $\eta_1 = \overline{\cos \phi_1}$ and $\epsilon = \overline{\sin \phi_1}$, and for the other

by $\eta_2 = \overline{\cos \phi_2}$ and $\overline{\sin \phi_2} = 0$. The expression is

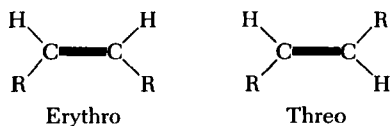
$$\bar{h}^2 = Nl^2 \frac{1 + \cos \alpha}{1 - \cos \alpha} \frac{1 - \eta_1 \eta_2}{(1 - \eta_1)(1 - \eta_2)} \times \frac{1 + \eta_1^2 \epsilon_1^2 / (1 - \eta_1 \eta_2)^2}{1 + \eta_2 \epsilon_1^2 / [(1 - \eta_1)(1 - \eta_1 \eta_2)]} \quad (5)$$

where N is the number of bonds, l the bond length, and $\alpha = \pi - \theta$, θ being the bond angle; this expression is valid for $N \gg 1$.

To calculate the dimensions for free rotation about the bonds connecting the monomeric units, let $\eta_2 = 0$, and assigning the tetrahedral angle value to α , the equation reduces to

$$\bar{h}^2 = 2Nl^2 / 1 - \eta_1$$

The fixed rotation angle about the bond of the monomer unit can assume either of two values, corresponding to the two possible stereoisomers which are represented in the following projection (for nomenclature see Ref. 15):



where the heavy line represents the acenaphthylene ring in a position perpendicular to the plane of the paper, the backbone carbons being in the plane and the four bonds above the plane; R represents adjacent monomer units. The respective values of η_1 for erythro and threo are -1 and $\frac{1}{2}$, and for ϵ , zero and $\sqrt{\frac{3}{2}}$ (by convention $\phi = 0$ for *trans*). Note that although $\epsilon = 0$ for threo, it does not affect the free-rotation dimensions. Thus we have

$$\bar{h}^2 = \begin{cases} Nl^2 & \text{for erythro} \\ 4Nl^2 & \text{for threo} \end{cases}$$

The corresponding well-known result for a paraffinic chain is $2Nl^2$.

Using these results we calculate free-rotation values for $(\bar{h}^2/M)^{1/2}$ of 180×10^{-11} for erythro and 360×10^{-11} for threo; these, along with the experimental results, yield theta-to-free-rotation ratios $\sigma = 3.3$ and 1.65 , respectively.

By appropriate substitutions in Eq. (5) we get $\eta_2 = 0.83$ for erythro and 0.80 for threo. On the basis of these results alone, one cannot favor either of the two isomers, although steric considerations make threo much more likely.

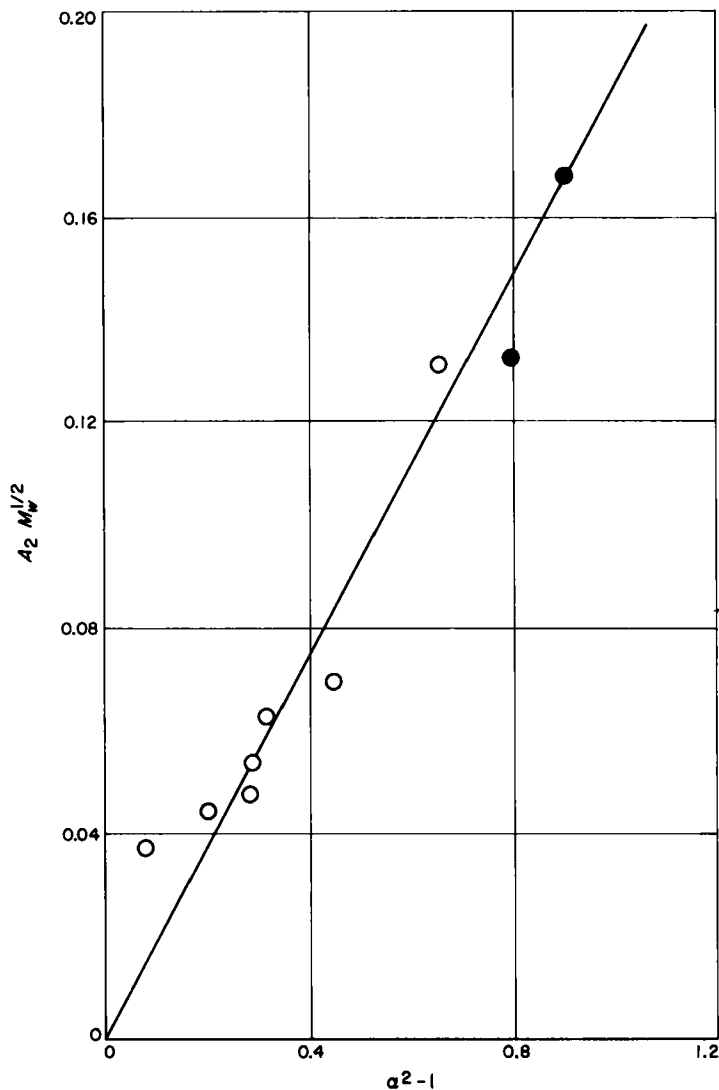


FIG. 8. Second virial coefficient plot according to Eq. (6).

To examine the behavior of PACN in a good solvent, we use the second virial coefficient, A_2 , data in benzene at 25°C. Recently Berry (21) showed that the first-order perturbation theory leads to

$$A_2 M^{1/2} = \frac{4N_A \pi^{3/2}}{a_1} (\bar{S}_0^2/M)^{3/2} (\alpha^2 - 1) + \dots \quad (6)$$

where N_A is Avogadro's number, $a_1 = \frac{135}{100}$, and \overline{S}_0^2 is the unperturbed mean-square radius of gyration. Data for polystyrene obtained over a wide range of α^2 could be represented using only the first term of Eq. (6) [see Berry (21)] i.e., $A_2M^{1/2}$ vs. $(\alpha^2 - 1)$ yields a straight line. We observe that the PAcN data shown in Fig. 8 are also linear. The expansion coefficient was estimated from $[\eta]/[\eta]_0 = \alpha_\eta^3 = \alpha^{5/2}$. Light-scattering measurements on the two high molecular weight polymers (filled symbols) gave an α^2 value 5–10% higher than those estimated from $[\eta]$ data; this discrepancy is within the accuracy of the experiments. The slope of the straight line gives

$$(\overline{h}_0^2/M)^{1/2} = 6^{1/2}(\overline{S}_0^2/M)^{1/2} = 638 \times 10^{-11}$$

in good agreement with the experimental values shown in Table 10.

Occurrence of branching during the thermal polymerization of acenaphthylene was suggested (11). Our results strongly suggest, however, that branching, if it occurs at all, cannot be extensive. The plot of $[\eta]$ vs. M_w (Fig. 4) is linear over a range of molecular weight from about 10,000 to 3,000,000. Moreover, the data shown in this figure were obtained on polymers prepared both in bulk and solution, with and without peroxide catalysts, and both low and high conversion. There is no trend which could be assigned to differences in polymerization conditions. Also all the results discussed above could be interpreted in terms of the behavior expected of linear polymers.

One exception was observed for a polymer prepared anionically whose M_w from light scattering was 3500 and M_v from Fig. 4 about 10,000. In spite of the difficulties with light scattering on low molecular weight polymers, this discrepancy seems to be beyond the probable experimental error. This difference may be caused by the erythro form being favored for ionic polymerization as suggested by Story and Canty (22); erythro would lead to dimensions about twice that of threo, as shown above.

CONCLUSIONS

One of the main conclusions of this work is that PAcN apparently exhibits considerable flexibility in solution. This is contrary to the extremely high degree of hindrance to rotation as indicated by examination of molecular models. The only plausible explanation is that even in solution PAcN must exhibit a considerable degree

of short-range order. Thus it is meaningless to speak of rotational potential about single bonds without considering nearest (and higher)-neighbor interactions. But for sufficiently long distances there are still enough degrees of freedom left for the chain to behave as a statistical coil. Short-range conformational order for polymers in solution seems more and more recognized to be as the rule rather than the exception (see, for example, Ref. 23). Thus, instead of saying that PACN is more flexible than we expected, it may be more appropriate to conclude that other polymers are less flexible than previously thought.

The apparent stereoregularity for PACN suggests that the placement of a monomer unit during polymerization can be dictated by steric factors even in the absence of stereo specific catalysts. The probable predominance of threo sequences was pointed out, but only more direct measurements, preferably on low molecular weight polymers, can resolve this question.

REFERENCES

1. K. Dziejowski and T. Stolyhow, *Ber.*, **57**, 1531 (1924).
2. R. G. Flowers and H. F. Miller, *J. Am. Chem. Soc.*, **69**, 1398 (1941).
3. M. Imoto and I. Soematsu, *Bull. Chem. Soc. Japan*, **1961**, 34.
4. M. Kaufman and A. F. Williams, *J. Appl. Chem.*, **1**, 489 (1951).
5. G. Mohorcic, *Bull. Sci. Conseil Acad. RPF Yugoslavie*, **3**, 105 (1957).
6. N. Vene and G. Mohorcic, *Rept. J. Setfan Inst. (Ljubljana)*, **5**, 71 (1958).
7. J. Moacanin, A. Rembaum, and R. K. Laudenslager, *Polymer Preprints*, **4**(2), 179 (1963); preprints of *Western Regional Meeting, ACS, Los Angeles, Calif., Nov. 1965*.
8. J. Springer, K. Ueberreiter, and R. Wenzel, *Makromol. Chem.*, **96**, 122 (1966).
9. J. Moacanin and A. Rembaum, *Polymer Letters*, **2**, 979 (1964).
10. C. S. H. Chen, *J. Polymer Sci.*, **62**, 38 (1962).
11. L. Utracki, N. Eliezer, and R. Simha, *Polymer Letters*, **5**, 137 (1967).
12. J. Springer, K. Ueberreiter, and R. Wenzel, *Makromol. Chem.*, **96**, 134 (1966).
13. M. C. Shen and A. Eisenberg, in *Progress in Solid State Chemistry*, Vol. 3 (H. Reiss, ed.), Pergamon Press, London, 1967.
14. J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373 (1958).
15. M. L. Huggins, G. Natta, V. Desreux, and H. Mark, *Makromol. Chem.*, **82**, 1 (1965).
16. M. Kurata and W. H. Stockmayer, *Fortsch. Hochpolym. Forsch.*, **3**, 196 (1963).
17. J. Brandeux and E. H. Immergut, *Polymer Handbook*, Wiley (Interscience), New York, 1966, pp. IV-161.
18. L. Utracki and R. Simha, *J. Polymer Sci.*, **A1**, 1089 (1963).
19. H. W. McCormick, *J. Colloid Sci.*, **16**, 635 (1961).

20. M. V. Volkenstein, *Configurational Statistics of Polymeric Chains*, Wiley (Interscience), New York, 1963, Chaps. 4 and 6.
21. G. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).
22. V. M. Story and G. Canty, *J. Res. Natl. Bur. Std.*, **68A**, 165 (1964).
23. T. M. Birshtein and D. B. Ptitsyn, *Conformations of Macromolecules*, Wiley (Interscience), New York, 1963, Chap. 8.
24. J. M. Cowie, D. J. Worsfold, and S. Bywater, *Trans. Faraday Soc.*, **1961**, 705.
25. V. N. Cvetkov, S. I. Klenin, S. A. Frenkel, O. V. Fomitcheva, and A. G. Zhuse, *Visokomolekul. Soedin.*, **4**, 540 (1962).

Zusammenfassung

Mehrere Polymerisationstechniken wurden untersucht, um hochmolekulare Polyacenaphthylene herzustellen. Thermische Polymerisation ergab Molekulargewichte von über 2,000,000.

Eine Anzahl von Polyacenaphthenfraktionen wurden durch Lichtstreuung, Osmotischen Druck und Viskosität in einem Theta-Lösungsmittel und in Benzol charakterisiert. Die folgenden Beziehungen zwischen grundmolarer Viskosität und Molekulargewicht wurden aufgestellt:

$$\begin{aligned} [\eta] &= 0.72 \times 10^{-4} \times M_w^{0.72} && \text{in Benzol bei } 25^\circ \\ [\eta] &= 4.56 \times 10^{-4} \times M_w^{0.50} && \text{in 1,2-Dichloräthan bei } 35^\circ \end{aligned}$$

Obwohl beträchtliche Behinderung der Rotationsbewegung von Kettensegmenten zu erwarten ist, konnte das Lösungsverhalten mit Hilfe der üblichen Zwei-Parametertheorie für flexible Ketten interpretiert werden. Die durch Lichtstreuung bestimmten Theta-Dimensionen stimmen mit den aus der grundmolaren Viskosität abgeschätzten Werten überein. Ausserdem waren diese Werte vergleichbar mit solchen des Polystyrols. Weiterhin ergab die Anwendung der erste Ordnung berücksichtigenden Störungstheorie zur Berechnung von zweiten Virialkoeffizienten annehmbare Radien für die Rotation. Der hohe Grad der Übereinstimmung der verschiedenen hier erhaltenen Messungen schliesst das Auftreten von Verzweigungsreaktionen während der thermischen Polymerisation aus.

Eine Betrachtung von Molekülmodellen zeigt, dass Threodiisotactizität die bei weitem wahrscheinlichste der vier möglichen Konfigurationen ist. Daher ergeben sterische Überlegungen zusammen mit der in allen Proben gefundenen Kristallinität Hinweise für eine beträchtliche Stereoregularität.

Résumé

On a étudié plusieurs techniques de polymérisation dans le but d'obtenir des polyacénaphthylènes à masses moléculaires élevées. On a trouvé que la polymérisation donne des masses moléculaires au-dessus de 2,000,000.

On a caractérisé un certain nombre des fractions de polyacénaphthylène par la diffraction de la lumière, la pression osmotique et les déterminations

de viscosité dans des solvants théta et dans le benzène. On a établi les rapports suivants entre la viscosité intrinsèque, poids moléculaire:

$$\begin{aligned} [\eta] &= 0.72 \times 10^{-4} \times M_w^{0.72} && \text{dans le benzène à } 25^\circ\text{C} \\ [\eta] &= 4.56 \times 10^{-4} \times M_w^{0.50} && \text{dans le 1,2-dichloroéthane à } 35^\circ\text{C} \end{aligned}$$

Malgré le fait qu'on s'attendait à l'empêchement considérable au mouvement rotationnel de segments de chaîne, le comportement de la solution a pu être interprété du point de vue des théories courantes à deux paramètres pour des chaînes flexibles. Les dimensions théta, déterminées par la diffusion de la lumière étaient en accord avec les valeurs obtenues de la viscosité intrinsèque et on les a trouvées comparables à celles du polystyrène. Aussi, l'application de la théorie de la perturbation du premier ordre aux données du deuxième coefficient virial a fourni des estimations raisonnables du rayon de gyration. Le degré élevé de cette stabilité interne parmi les différentes mesures exclut l'occurrence des réactions de branchement significatives au cours de la polymérisation thermique.

L'examen des modèles moléculaires indique que la configuration threo-diisotactique est de loin la plus probable parmi les quatre stéréo configurations possibles. Ainsi, des considérations stériques ensemble avec la cristallinité observée dans tous les échantillons étudiés suggèrent une stéréoregularité considérable.

Received by editor May 20, 1967

Submitted for publication August 18, 1967