Polyisocyanate 류의 용액물성에 관한 연구 Ⅱ 희박용액 중에서의 n-Hexyl-p-Tolylisocyanate 공중합체의 분자형태

김 영 철 · 이 동 주

인하대학교 고분자공학과

(1979년 2월 13일 접수)

Dilute Solution Properties of Polyisocyanates II. Conformational Behavior of n-Hexyl-p-Tolylisocyanate copolymer in Dilute Solution.

Yong Chul, Kim & Dong Choo, Lee

Dept. of Polymer Science and Technology, Inha University, Inchon, Korea

(Received February 13, 1979)

要約 : 저온 음이온 중합법에 의하여 n-Hexyl isocyanate 단중합체, p-Tolyl isocyanate 단중합체 및 p-Tolyl isocyanate 함량이 16몰 퍼센트되는 n-hexyl isocyanate 공중합체를 합성하였다. 이들 각 중합체들을 연속식 재 침전 방법으로 분자량분포가 비교적 좁은 분별물로 분별하였다. 각 분별시료에 대하여 수평균분자량($\overline{Mn}$)과 제 2 virial 계수 (A^2)를 37°C 에서 삼투압 측정으로 결정하였다. 분자량 2.9×10^4 에서 7.3×10^5 g/mole 에 해당되는 분별시료들의 극한 점도를 Toluene, Chloroform, Tetrahydrofuran 등을 용매로하여 θ-온도 및 25°C 에서 측정하였다. Toluene 을 용매로 하는 상분리 실험을 하여 n-Hexyl isocyanate 단중합체의 θ-온도가 14.8°C 및 공중합체의 θ-온도가 13.2°C 임을 밝혔다.

25°C 에서의 극한 점도값 및 37°C 에서의 제 2 Virial 계수값들을 기초로하여 몇가지 외삽법에 의한 수단으로 각 중합체의 Toluene 중에서의 이상분자(理想分子) 크기를 결정 비교하였다.

공중합체의 단거리상호작용 Parameter 값은 1.200×10^{-8} cm·mole$^{1/2}$/g$^{1/2}$ 로 밝혀졌으며 이것은 p-Tolyl isocyanate 은중합체의 값과 비슷하였고 n-Hexyl isocyanate 단중합체 값보다는 훨씬 적은 것으로 나타났다. 이들 결과와 공중합체의 반응성 비의 값들로 부터 n-Hexyl-p-Tolyl isocyanate 공중합체의 Toluene 중 이상분자 형태가 n-Hexyl 단위가 짧게 연결된 Interrupted helix 구조인 것으로 추정되었다.

김 영 철 · 이 동 주

Abstract : The poly(n-hexyl isocyanate), poly(p-tolyl isocyanate), and copoly (n-hexyl-p-tolyl isocyanate) which contains 16 mole percent of p-tolyl isocyanate content have been prepared by low temperature anionic polymerization in dimethyl formamide. Narrow-distribution fractions of each polymer species were obtained by carefully controlled successive fractional precipitation method. Number average molecular weight($\overline{M}n$) and osmotic second virial coefficients were determined by osmometry in toluene at 37°C. The intrinsic viscosity behaviors of each series of polymer fractions have been examined over the molecular weight range of 2.9×10^4 to 7.3×10^5 g/mole in toluene, chloroform, and tetrahydrofuran at 25°C, as well as under theta conditions. Thetatemperatures of 16.4°C for poly(n-hexyl isocyanate), 14.8°C for poly(p-tolyl isocyanate), and 13.2°C for the copolymer of n-hexyl and p-tolyl isocyanate were obtained from the phase separation studies in toluene. The unperturbed molecnlar dimensions in dilute toluene solution have been determined by a number of extrapolation methods for data at 25°C. The value of short-range interaction parameter, $A = (<R^2>_0/Mn)^{1/2}$, of copolymer was found as $1.200 \times 10^{-8} cm \cdot mol^{1/2}/g^{1/2}$. This was comparable with the value obtained for poly(p-tolyl isocyanate), $1.11_4 \times 10^{-8}$, but was found to be far below than that of poly(n-hexyl isocyanate), 3.24×10^{-8}. The molecular shape of copolymer in toluene at theta condition, therefore, was estimated as a interrupted helix structure with short blocks of n-hexyl isocyanate units.

Introduction

High molecular weight polyisocyanates have aroused considerable interest on their unusual properties in dilute solution since their original preparation over a decade ago. The chain stiffness of poly(n-alkly isocyanate)(n-PAIC) was first suggested by Tietz[1] et al. who had found abnormally high intrinsic viscosities for relatively low molecular weight samples and unusually high melting points in spite of the absence of hydrogen bond. This inference regarding chain stiffness was substantiated by the experimental results of Buchard[2] on poly(n-butyl isocyanate)(n-PBIC) samples. His measurements on the solution properties of his samples showed that both the viscosity-molecular weight exponent and the sedimen-tation coefficient-molecular weight exponent appear to lie outside the range expected for Gaussian behavior.

An early light scattering study by Schneider et al[3]. on poly(n-hexyl isocyanate) (n-PHIC) confimred directly that the n-PHIC molecules exhibit extraordinarily high radii of gyration. Fetters et al[4]. also proposed the chain rigidity of n-PAIC by analyzing the molecular dependence of the osmotic second virial coefficients and the radii of gyration in terms of the wormlike-coil model of Kratky and Porod. In their recent work on n-PBIC, Ambler et al[5]. disclosed that the low molecular weight($<10^5$) polymer exhibited rod-like behavior while the high molecular weight(10^7) samples appeared to be essentially that of a wormlike chain in tetrahydrofuran(THF) and chloroform.

Though the origin of the chain stiffness of the n-PAIC is at present not totally clear, but basically, the conformation of n-PAIC has been described by most authors as being helical and rigid at low molecular weight.

One further interesting point with regard to the chain stiffness of polyisocyanate is the observation of the molecular posture of poly(aromatic isocyanate). A random coil conformation of poly(p-tolyl isocyanate) (p-PTIC) in bromoform has been confirmed by Tsvetkov[6] and a chemical basis for this has been suggested that the possibility of partial double bond character imposing coplanarity along the backbone may be diminished due mainly to the resonance hybridzation of aromatic ring.

It is, therefore, desired to prepare a copolymer of n-hexyl and p-tolyl isocyanate(H-TPIC) for purpose of observing the conformational change of hexyl units by inserting a low quantity of tolyl units in the main chain of hexyl homopolymer. Copolymers were prepared by the method proposed by Lee.[7] Careful measurements of osmotic pressure and intrinsic viscosity were made on sharply fractionated samples, ranging in molecular weight from 2.9×10^4 to 7.3×10^5 g/mole, in toluene, THF, and chloroform. The unperturbed molecular dimensions in idilute toluene solution were determined by the various extrapolation methods for data at 25°C, and the value of short-range interaction parameter of H-TPIC under theta(θ) condition was compared with those of its parents homopolymers.

Experimental

1) Monomers and initiator: n-Hexyl isocyanate(n-HIC) and p-tolyl isocyanate(p-TIC) of technical grades from the Eastman Org. Chemicals Co. were distilled under reduced nitrogen atmosphere after drying overnight over calcium hydride(b.p. 67°C for n-HIC at 30 mmHg and 95°C for p-TIC at 38 mmHg).

Chemically pure soldium cyanide from the Wako Chemicals Co. was pruified by three times of recrystallization from water.

2) Polymer samples: Polymers were prepared by the Shashoua's method[1]. Detailed discussions of the procedures used in their synthesis have been given[7]. All the polymer samples obtained were purified by conducting several cycles of solubilization in toluene and reprecipitation in methanol. They were finally dried under reduced pressure at room temperature. Table I summarizes the polymerization data.

3) Solvents: Dimethyl formamide(DMF) was distilled under reduced pressure immediately before using, after drying over molecular sieves(b.p. 59°C at 30mmHg). Toluene of reagent grade was shaken with concentrated sulfuric acid, washed with 0.1 N NaOH and water several times successively, and drived over metallic sodium. It was then distilled under atmosphere(b.p. 110.5°C). Chloroform of reagent grade was also treated with concentrated sulfuric acid, washed with water, and dried over anhydrous sodium sulfate. It was then purified by simple distillation(b.p. 61.2°C). After drying over litium aluminum tetrahydride, THF was distilled under atmosphere(b.p. 66°C). Methanol and n-hexane were purified by simple distillation(b.p. 64.7 and 67.5°C, respectively).

4) Fractionations of polymer samples: A dilute solution(0.5% w/v) of polymer sample in good solvent was placed in a 3l fractionation vessel in a thermostat at 20°C. After equilibration, nonsolvent was added so as to
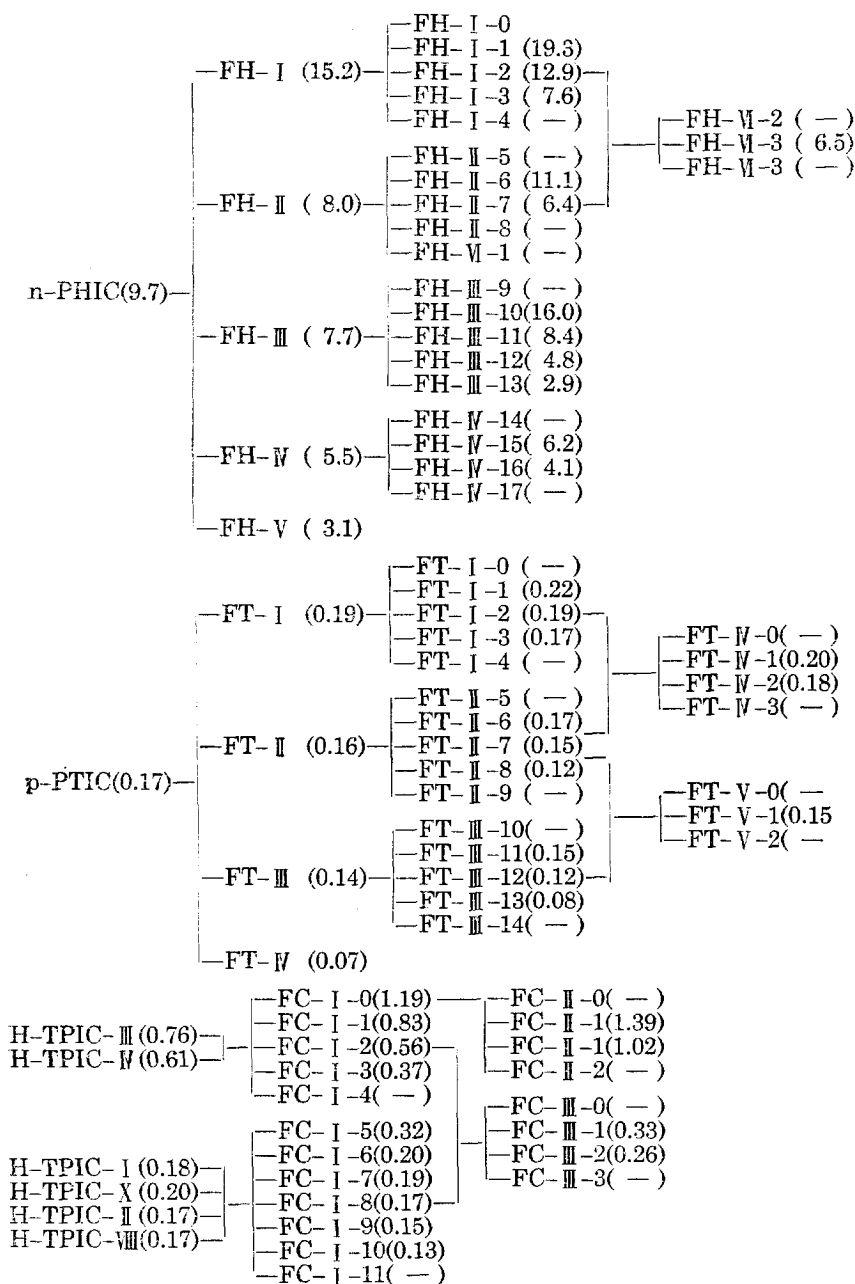
Figure 1. Schematic diagrams of the refractionation procedure. (numbers in parentheses denote [η] in toluene at 25°C).

the nonsolvent directs into the vortex created by the stirrer until the solution became permanently turbid, the temperature was then raised to 10–15°C above the fractionation temperature and maintained there with stirring until homogeneity was reached. When temperature eqilibrium was reached the stirring was stopped and the system was left to settle slowly. The temperature was then slowly lowered to 20°C. After settling

overnight the clear supernatant was rapidly decanted off and the precipitate was redissolved in good solvent and reprecipitated by dropwise addition of the solution to methanol. In this manner, eight fractions of p-PTIC, eleven fractions of n-PHIC, and also eleven fractions of H-TPIC were obtained. The solvent-nonsolvent system used for the fractionation of n-PHIC was toluene-methanol, and for the p-PTIC and H-TPIC were THF-n-hexane. The schematic diagrams of the refractionation procedure of each series of polymers were illustrated in Fig. 1.

5) **Osmometry:** The number average molecular weight($\overline{M}n$) and second virial coefficient(A_2) were obtained from osmotic pressure measurements using a high speed membrane osmometer, Hewlett Packard Model 501, fitted with "membrane 08". Measurements were made in toluene at 37°C and results were interpreted by the procedure of Berglund[8].

6) **Viscometry:** Intrinsic viscosity, $[\eta]$, was measured in toluene, chloroform, and THF, respectively, at 25°C, and in toluene under θ-condition. The viscometers used were of the Ubbelohde suspended level type designed to have flow times of about 200 sec. for the solvents. End effect and kinetic energy corrections were all negligible, additionally, shear effects were absent from all measurements. The Huggins plot[9] and the Mead-Fuoss plot[10] were combined to determine intrinsic viscosity.

7) **Partial specific volume:** The densities of polymer solution and solvent at 30°V were measured by use of a pycnometer of 30ml. capacity. The buoyancy factor $1-\bar{v}\rho_0$ was estimated from the slope of a plot of solution density versus polymer concentration. The partial specific volume of the polymer was computed from the value of buoyancy factor.

8) **Phase separation:** Critical solution temperatures were determined for three fractions of each polymer in toluene. Initial solutions were prepared with polymer concentrations approximately twice the critical volume fraction . In each measurement, abut 5ml of solution was sealed in a glass tube. The tube was immersed in a bath, first kept at about 60°C. The temperature was gradually lowered at a rate of about 1°C/min., while the solution was being constantly shaken. The temperature at which an incipient cloudiness was recognized by visual inspection was recorded as the precipitation temperature. The disappearance of cloudiness upon rewarming was also checked as the dissolution temperature. The results were analyzed by the Flory-Shultz equations[11][12].

9) **Differential scanning calorimetry:** Thermal transitions of polymers were measured using Perkin-Elmer DSC-1B, under air and with scan speed 5°C/min.. The temperature calibration was performed with Indium.

Results & Discussion

Copolymer.

Copolymerization was proceeded in a homogeneous phase as the case of homopolymerization. The comonomer feed was so controlled as to contain 16 mole percent of p-tolyl isocyanate content in the copolymer composition[7]. The resulting polymer, being found as a white powder, was subjected to thermal transitions measurements by using a differential scanning calorimeter, after the copolymer was throughly purified.

Thermal transition temperatures of each polymer are summarized in the last column of Table I. As is evidenced from the data in Table I, the decomposition point of copolyer is quite distinctive from its parents

Table I. Polymerization Data of Homo-and Copolymer

Polymer	Monomer (gr.)	DMF (ml.)	Initiator[a] (ml.)	Yield (%) K[b]	Yield (%) S[c]	$[\eta]$[d] (dl/g)	DSC[e] (Temp. °C)
p–PTIC	4.02	30.0	0.6	57.3	25.0	0.237	193
n–PHIC	5.37	40.0	1.2	67.8	85.0	9.689	195.2
H–TPIC	3.25 (p–TIC) 2.04 (n–HIC)	35.0	0.85	54.5	—	0.761	200

a: NaCN in DMF (0.32 mole/1)
b: Data obtained from this work
c: Data obtained Shashowa's work
d: Measured in toluene at 25°C
e: Thermal transition temperature by DSC.

homopolymers. This confirmed quantitatively that the copolymer was purified satisfactorily.

According to the Lee's data[7] on the reactivity ratio of this copolymer system($r_1=0.55$ for p–TIC and $r_2=16.7$ for n–HIC), the selectivity of n–HIC toward the two reacting species in DMF is considered obviously greater than the p–TIC, that is the behavior of anionic copolymerization of this comonomer pair is rather the type of less ideal.

Molecular weight and second virial coeffient.

According to the theory of dilute polymer solutions, the osmotic pressure may be expressed as a function of the concentration by an equation of the form[8].

$$(\pi/RTc)^{1/2}=1/(Mn)^{1/2}(1+A_2Mn\ c/2+\ldots)$$

where π is the osmotic pressure, c is the polymer concentration in g/dl, R is the gas constant, T is the absolute temperature, and A_2 is the second virial coefficient. The value of $\overline{Mn}$ was determined from the intercept of the straight line of the plot$(\pi/RTc)^{1/2}$ versus concentration and the value of A_2 was derived from the slope of the straight line. Fig. 2,3, and 4 illustrate the plots of$(\pi/RTc)^{1/2}$ vs. c for each series of polymer fractions.

The data points for each fractions are closely fitted by a straight line and allow an accurate evaluation of $\overline{Mn}$ and A_2. Values of $\overline{Mn}$ are given in Table II, also included are A_2. As is shown in Table II, $\overline{Mn}$ values are all relatively low. This is considered to be due mainly to the impurities existed in the polymerization system.

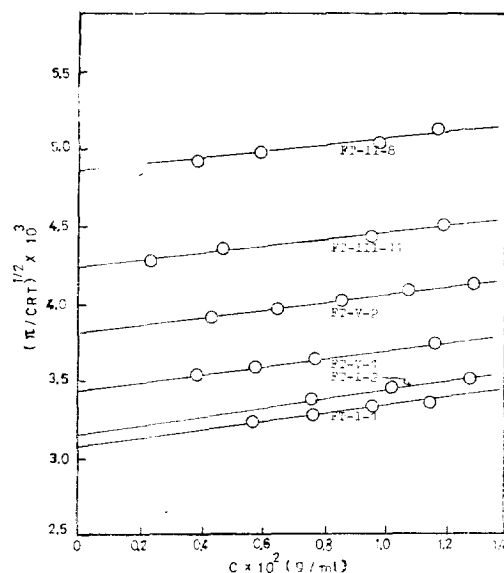In the point of view, however, that the conformational behavior of polyalkyl isocy-

Figure 2. Square root of reduced osmotic pressure as a function of polymer concentration for p-PTIC in toluene at 37 C.
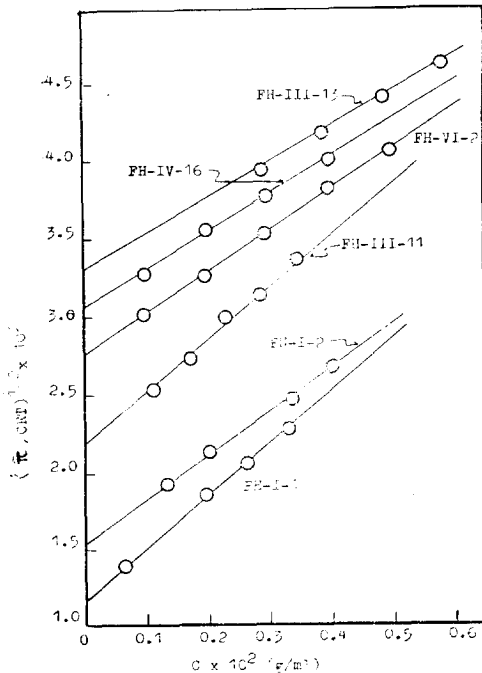
Figure 3. Square root of reduced osmotic pressure as a function of polymer concentration for n–PHIC in toluene at 37°C.
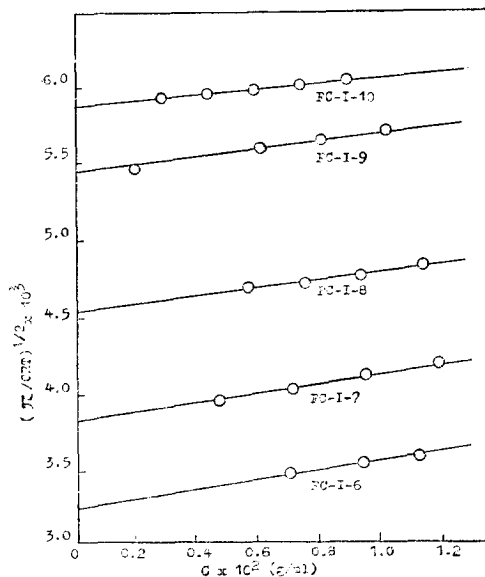

Figure 4. Square root of reduced osmotic pressure as a function of polymer concentration for H–TPIC in toluene at 37°C.

Table Ⅱ. Values of $\bar{M}n$ and Osmotic Second Virial Coefficients of Each Polymer Fraction, Measured in Toluene at 37°C.

Polymer	Fraction	$\bar{M}n \times 10^{-4}$ (g/mol)	$A_2 \times 10^4$ (ml. mol/g²)
	FT–I–1	10.75	1.58
	FT–I–2	10.08	1.63
p–PTIC	FT–V–1	8.50	1.69
	FT–V–2	6.89	1.73
	FT–Ⅲ–11	5.56	1.75
	FT–Ⅱ–8	4.20	1.80
	FH–I–1	71.82	7.92
	FH–I–2	41.62	8.64
n–PHIC	FH–Ⅲ–11	20.66	14.50
	FH–Ⅵ–2	13.22	14.69
	FH–Ⅳ–16	10.68	14.68
	FH–Ⅲ–13	9.18	14.71
	FC–I–6	9.47	1.95
	FC–I–7	6.82	2.15
H–TPIC	FC–I–8	4.85	2.18
	FC–I–9	3.35	2.26
	FC–I–10	2.90	2.30

anate in dilute solution is clearly rodlike[5] when its molecular weight is relatively low ($<10^5$), the $\bar{M}n$ values obtained here are belived to be enough to find out the conformational difference between poly alkyl and poly aryl–alkyl isocyanate.

Flory and Krigbaum[13] developed an approximate theory on the second virial coefficient by using a Gaussian chain model, that the value of A_2 in a given solvent and at a given temperaute falls as the molecular weight of a polymer comprising flexible coil molecules rises. This prediction was qualitatively in accord with experimental results. In Table II, values of A_2 of p–PTIC and H–TPIC, which are showing quite lower values than those of n–PHIC fractions, are appeared to be decreased as the molecular weight rises. This change in A_2 of the two polymers (p–PTIC and H–TPIC) was belived to be certainly an indication that both the polymers are flexible coil molecules in toluene.

For rigid rodlike macromolecules, on the other hand, it has been known[14, 15, 16] that A_2 is not only independent on molecular weight and solvent power but also constant in value with molecular weight, at least in a given solvent and below an upper limit of molecular weight. Fetters et al[16]. demonstrated the independence of the osmotic second virial coefficient of n–PHIC on molecular weight and the constancy of $A_2(21.5 \times 10^{-4}$ mol.ml.g$^{-2})$ for a tenfold range of molecular weight below Mn 2.7×10^5. A lower average value of osmotic A_2 $(8.0 \times 10^{-4}$ mol.ml.g$^{-2})$ for n–PHIC has also been reported elsewhere[17].

Values of A_2 for the n–PHIC in Table II. show no dependence on the molecular weight below 2.07×10^5 and are showing their constancy with the molecular weight. Although there is some disagreement on A_2 values with other workers, it seems quite legitimate to take the numerical results of A_2 as an evid-
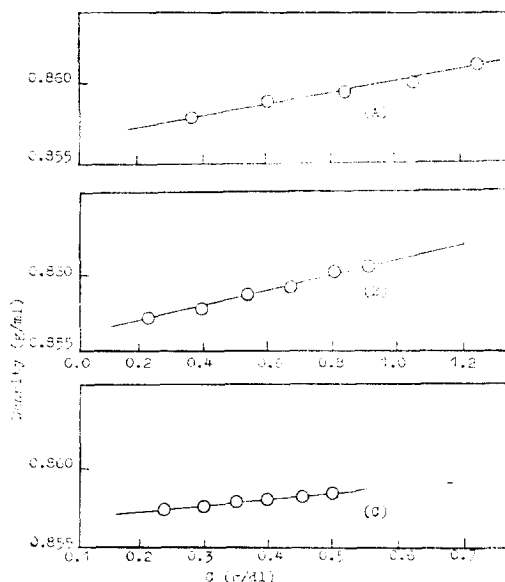

Figure 5. Plot of solution density vs. polymer concentration, in toluene at 30°C. (A): p–PTIC, M̄n=9.02×10⁴ (B): H–TPIC, M̄n=9.07×10⁴ (C): n–PHIC, M̄n =10.6×10⁴.

Table Ⅲ. Values of Partial Specific Volumes and Critial solution Temperatures of Polymer Fractions, Determined by The Phase Separation Studies.

Sample code	v̄(cm⁴/g)	T_c(°C)
FT–I–1	0.790	16.9
FT–I–2	—	—
FT–V–1	0.761	11.2
FT–V–2	0.807	12.0
FT–Ⅲ–11	0.703	—
FT–Ⅱ–8	0.791	12.5
FH–I–1	0.970	—
FH–I–2	0.879	14.5
FH–Ⅲ–11	1.051	15.0
FH–Ⅵ–2	1.045	13.2
FH–Ⅵ–16	0.912	13.4
FC–I–6	0.805	11.9
FC–I–7	0.776	10.0
FC–I–9	—	9.8
FC–I–10	0.785	10.7

ence for a rodlike nature of the n–PHIC chain in dilute toluene solution.

Phase separation (upper critical solution temp.)

In Fig. 5 have been illustrated the representative plots of solution density versus concentration of samples of selected fraction from the polymer species concerned. The experimental data gave straight lines in the range of concentrations studied. Values of v̄ computed from the slope of the straight lines were summarized in Table Ⅲ, and with these v̄ values the theoritical critical volumes were evaluated by an equation[18] of the form

$$\phi = 1/x^{1/2}$$

$$x = M \bar{v}/v_o$$

where v̄ is the partial specific volume of the polymer and v̄ is the molar volume of solvent.

Temperatures at which precipitation occurs on cooling toluene solutions of three fractions of each polymer species investigated are shown by the points plotted against the critical volume in Fig. 6 to 8. It is worth
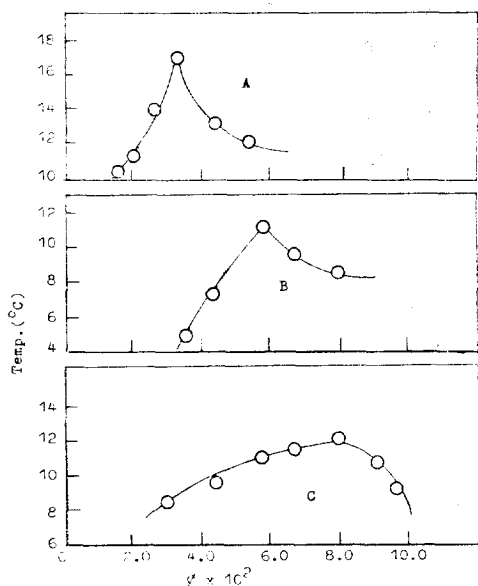
Figure 6. Phase separation curves of p–PTIC fractions in toluene.
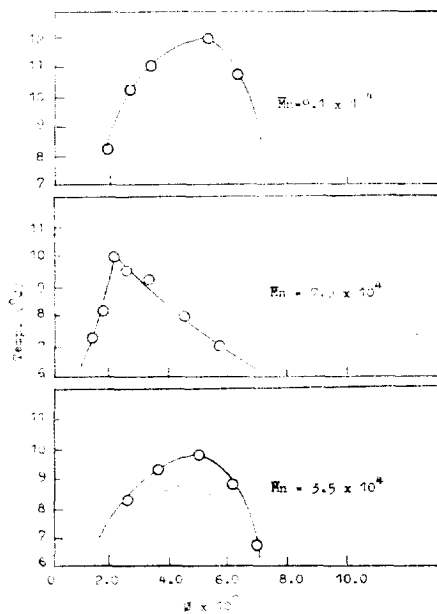A: $\bar{M}n=10.4\times10^4$ B: $\bar{M}n=9.0\times10^4$
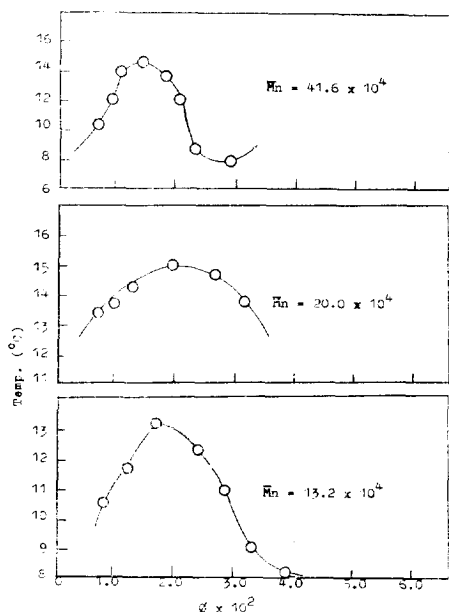C: $\bar{M}n=6.9\times10^4$

Figure 7. Phase separation curves of n–PHIC fractions in toluene.

remarking that the critical volume fractions of n–PHIC at where the maximum precipitation temperatures appeared are quite lower

Figure 8. Phase separation curves of H–TPIC fractions in toluene.

than those of p–PTIC or H–TPIC. This phenomenon is well agreed with the fact[19] that the consolute point(at which the difference between two coexisting phases vanishes) will occur in a very dilute system if the polymer chains are very long.

All the curves in the figures on phase diagrams are showing striking dissymmetry, which is not normally found in binary systems of simple liquids. This was considered to be due to the great disparity in the sizes of the molecules of the two components.

The maximum points in the phase diagrams, representing the critical solution temperature T_C, are also included in Table III. The general trend was that the higher T_C was found at the higher molecular weight in the same series of fractions. This characteristic, which is typical of systems consisting of a polymer fraction in a single solvent component, is also confirmed by many workers[20, 21].
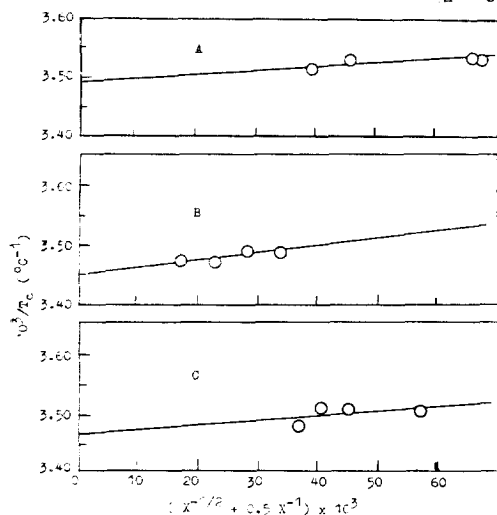
Figure 9. Flory–Shultz plots for polymers in toluene.
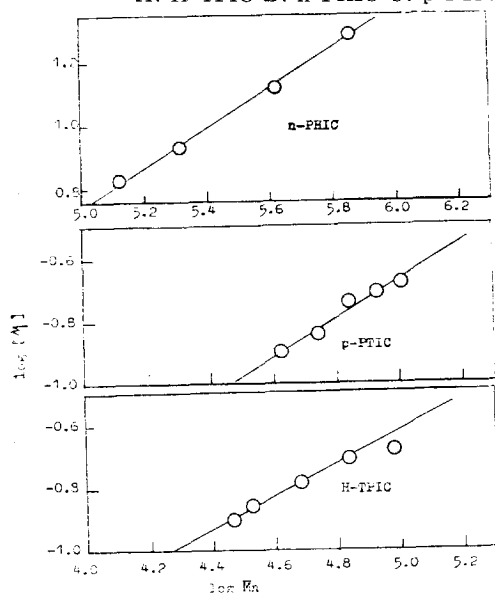A: H–TPIC B: n–PHIC C: p–PTIC

Figure 10. Molecular weight dependence of intrinsic viscosity in toluene at θ–temperature.

Theta temperatures.

Reciprocals of the critical temperatures, i.e. the maxima in the phase diagrams, are plotted in Fig. 9 against the function $1/x^{1/2}+1/2x$, according to the Flory–Shultz equation in the form[20] of

$$1/T_C = 1/\theta[1+(1\varPsi)\,(x^{-1/2}+x^{-1}/2]$$

where T_C is the critical solution temperature in degress Kelvin, θ is the theta or Flory temperature, $\varPsi$ is the Flory entropy parameter, and, $\times$ is the Mv/v_0. Experimental data are accurately linear within experimental error. From the intercepts of the straight lines in Fig. 9, θ–temperatures of 16.4°C for n–PHIC, 14.8°C, for p–PTIC, and 13.2°C for H–TPIC were obtained. Although the exponent α of Mark–Houwink equation confirms the above temperatures as the θ–temperatures(see the Intrinsic viscosity), the maximum temperature may not correspond exactly to T_C. Consequently, it was expected that the real θ–temperatures of n–PHIC and H–TPIC may be slightly lower than those quoted here, whereas the θ–temperature of p–PTIC may be slightly higher than that obtained.

Intrinsic viscosity.

The molecular weight dependences of intrinsic viscosity of polymers in toluene at θ–temperature are shown in Fig. 10. Straight lines have been drawn through the double logrithmic plots of Mark–Houwink relation. The values of Mark–Houwink constants, K and α, obtained from the intercepts and slopes

Table Ⅳ. List of Mark–Houwink Constants, $[\eta]=KMn^{\alpha}$, of Polymer Species Studied in Various Solvents.

Solvent	Temp. (°C)	n–PHIC		p–PTIC		H–TPIC	
		$K\times10^4$	α	$K\times10^4$	α	$K\times10^4$	α
Toluene	T_θ	39.47	0.62	5.67	0.51	7.93	0.50
	25	34.48	0.64	5.94	0.52	2.30	0.61
Chloroform	25	2.80	0.82	1.91	0.66	0.98	0.73
T.H.F.	25	0.009	1.12	6.50	0.71	0.66	0.72

For rigid rodlike macromolecules, on the other hand, it has been known[14,15,16] that A_2 is not only independent on molecular weight and solvent power but also constant in value with molecular weight, at least in a given solvent and below an upper limit of molecular weight. Fetters et al[16]. demonstrated the independence of the osmotic second virial coefficient of n–PHIC on molecular weight and the constancy of $A_2(21.5\times10^{-4}$ mol.ml.g^{-2}) for a tenfold range of molecular weight below Mn 2.7×10^5. A lower average value of osmotic A_2 $(8.0\times10^{-4}$ mol.ml.g$^{-2})$ for n–PHIC has also been reported elsewhere[17].

Values of A_2 for the n–PHIC in Table II. show no dependence on the molecular weight below 2.07×10^5 and are showing their constancy with the molecular weight. Although there is some disagreement on A_2 values with other workers, it seems quite legitimate to take the numerical results of A_2 as an evid-
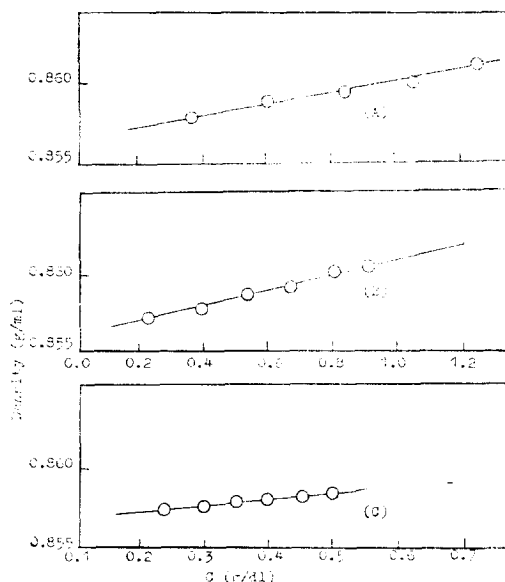
Table Ⅲ. Values of Partial Specific Volumes and Critial solution Temperatures of Polymer Fractions, Determined by The Phase Separation Studies.

Sample code	$\bar{v}(cm^4/g)$	$T_c(°C)$
FT-I-1	0.790	16.9
FT-I-2	—	—
FT-V-1	0.761	11.2
FT-V-2	0.807	12.0
FT-Ⅲ-11	0.703	—
FT-Ⅱ-8	0.791	12.5
FH-I-1	0.970	—
FH-I-2	0.879	14.5
FH-Ⅲ-11	1.051	15.0
FH-Ⅵ-2	1.045	13.2
FH-Ⅵ-16	0.912	13.4
FC-I-6	0.805	11.9
FC-I-7	0.776	10.0
FC-I-9	—	9.8
FC-I-10	0.785	10.7

ence for a rodlike nature of the n–PHIC chain in dilute toluene solution.

Phase separation (upper critical solution temp.)

In Fig. 5 have been illustrated the representative plots of solution density versus concentration of samples of selected fraction from the polymer species concerned. The experimental data gave straight lines in the range of concentrations studied. Values of $\bar{v}$ computed from the slope of the straight lines were summarized in Table Ⅲ, and with these $\bar{v}$ values the theoritical critical volumes were evaluated by an equation[18] of the form

$$\dot{\phi}=1/x^{1/2}$$
$$x=M \bar{v}/v_0$$

where $\bar{v}$ is the partial specific volume of the polymer and $\bar{v}$ is the molar volume of solvent.

Temperatures at which precipitation occurs on cooling toluene solutions of three fractions of each polymer species investigated are shown by the points plotted against the critical volume in Fig. 6 to 8. It is worth

Figure 5. Plot of solution density vs. polymer concentration, in toluene at 30°C. (A): p–PTIC, $\bar{M}n=9.02\times10^4$ (B): H–TPIC, $\bar{M}n=9.07\times10^4$ (C): n–PHIC, $\bar{M}n=10.6\times10^4$.

of straight lines in Fig. 10 are listed in Table IV.

The demonstration that the α values of p-PTIC and H-TPIC have been approached closely to the theoretical slope of one-half offers solid support of θ-conditions. This provides also an evidence that the molecules of both the polymers take their conformation in toluene as random coil. On the other hand, the deviation of α value of n-PHIC from the theoretical value 0.5 at θ-state was suspected to be due possibly to the original chain stiffness of molecules of n-PHIC. For the two solvents, chloroform and THF, α values of n-PHIC were 0.82 and 1.12, respectively. These are slightly less than that expected for rodlike chains but a comparison with the values of p-PTIC and H-TPIC make it certain that the chains of n-PHIC posses more extended posture than eigher of the former two polymers.

Unperturbed molecular dimensions.

Two principal methods, which are operative in very dilute solutions only, are generally in use for determining unperturbed molecular dimensions of macromolecules. One depends upon determination of the unperturbed mean-square radius $\langle S^2 \rangle_0$, which is one of the two basic molecular parameters representing short range interferences in the chain, by light scattering measurements at θ-temperature. The other involves the determination of the intrinsic viscosity-molecular weight relationship, from which the mean square end to end distance $\langle R^2 \rangle_0$ can be obtained.

As it was impossible to use method using light scattering measurements here, the unperturbed dimensions were estimated by several indirect or extrapolation methods which are using intrinsic viscosity-molecuar weight data.

According to Flory-Fox, [3,22,23] intrinsic viscosity is expressed in the form

$$[\eta] = K_0 M^{1/2} \alpha_\eta^3$$

with

$$K_0 = \Phi_0 A^3$$
$$A^2 = \langle R^2 \rangle_0 / M$$

where α_η is the expansion factor, Φ_0 is the Flory viscosity constant, and A is the short-range interaction parameter. The equation cited above suggests that measurements of intrinsic viscosities for various molecular weights yield values of K_0, from which the parameter A can be estimated when the value of the viscosity constant Φ_0 were presented[24], it has been adopted here a value of 0.42×10^{21} cgs. which has been calculated by Schneider et al.[3] with the n-PBIC sample under θ-condition.

Numerous procedures of estimating parameter A are available and have been reviewed by Yamakawa[25] and Cowie[26]. Five extrapolation methods have been used here.

*Modified Stockmayer-Fixman plot[25] (I)

$$[\eta]/M^{1/2} = 1.05K_0 + 0.287\Phi_0 BM^{1/2}$$

with

$$B = \beta/M_s^2$$

where β is the binary cluster intergral and the M_s is the molecular weight of the segment.

*Berry viscosity plot[27] (II)

$$([\eta]/M^{1/2})^{1/2} = K_0^{1/2} + 0.42K_0^{1/2}\Phi_0 BM/[\eta]$$

*Inagaki-Ptitsyn plot[25] (III)

$$[\eta]^{4/5}/M^{2/5} = 0.786K_0^{4/5}$$
$$+ 0.454K_0^{2/15}\Phi_0^{2/3}B^{2/3}M^{1/3}$$

*Kurata plot[28] (IV)

$$A_2 M^{1/2} = 1.65 \times 10^{23} \ A^3 + 0.968 \times 10^{23} BM^{1/2}$$

where A_2 is the second virial coefficient.

*Baumann plot[29] (V)

$$(\langle R^2 \rangle_0/M)^{3/2} = A + BM^{1/2}$$

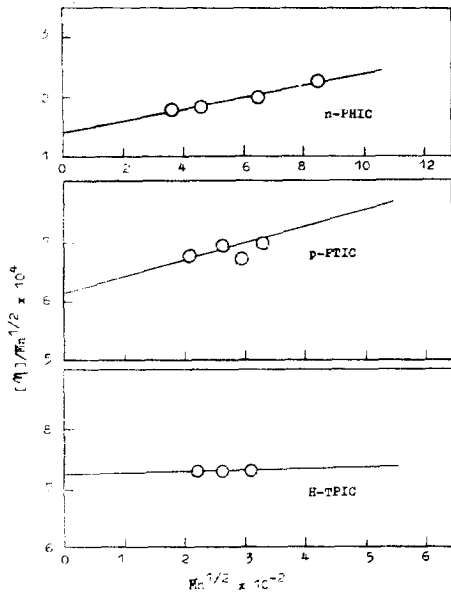Methods (I) to (III) used intrinsic viscosity data in dl/g at 25°C in toluene, and method

Figure 11. The modified Stockmayer–Fixman plots. Intrinsic viscosity data measured in toluene at 25°C are used. Units omitted to simplify appearance.
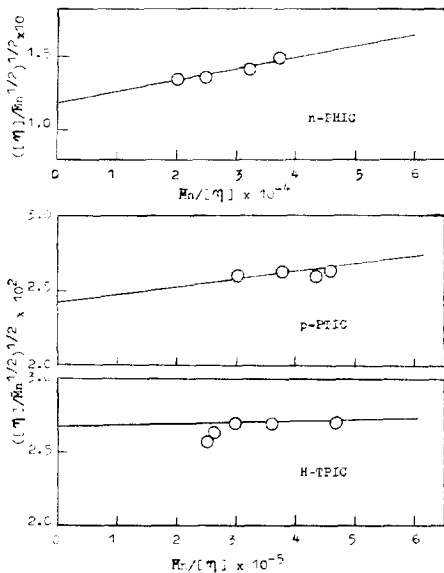

Figure 13. The Inagaki–Ptisyn plots. Intrinsic viscosity data measured in toluene at 25°C are used. Units omitted to simplify appearance.

Figure 12. The Berry viscosity plots. Intrinsic viscosity data measured in toluene at 25°C are used. Units omitted to simplify appearance.
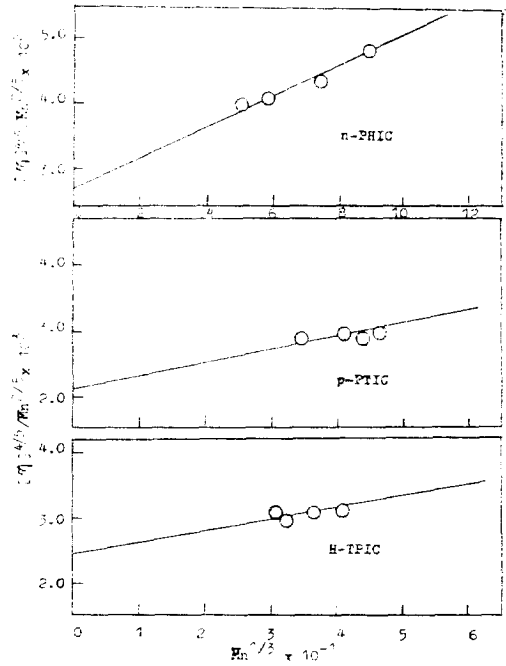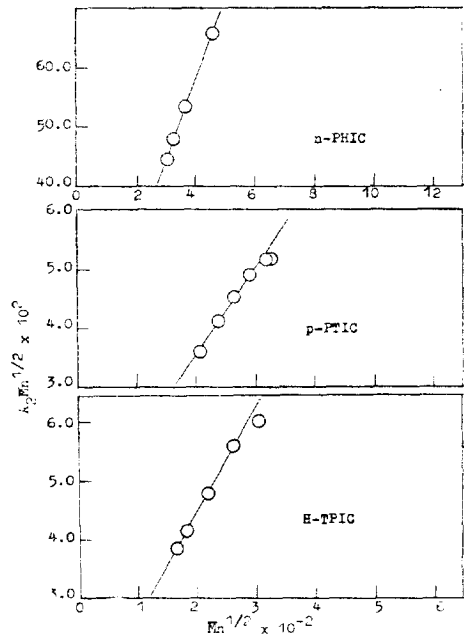

Figure 14. The Kurata plots. The osmotic second virial coefficients measured in toluene at 37°C are used. Units omitted to simplify appearance.
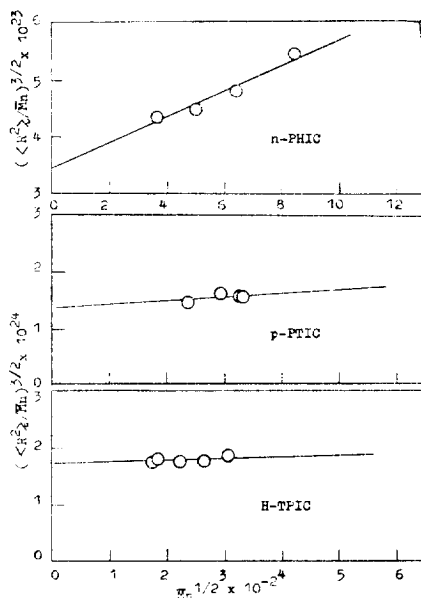
Figure 15. The Bauman plots. Units omitted to simplify appearance.

Table V. Values of Short-Range Interaction Parameters, $A = (\langle R^2 \rangle_0 / M)^{1/2}$, of Polymer Species Studied in Toluene at 25°C from Various Extrapolation Methods.

Polymer	Plot	$A \times 10^8$ (cm. mol$^{1/2}$/g$^{1/2}$)	Average[a]
	Kurata	0.534	
	Baumann	3.271	
n-PHIC	Stockmayer	3.204	3.241
	Berry	3.212	
	Inagaki	3.278	
	Kurata	0.308	
	Baumann	1.113	
p-PTIC	Stockmayer	1.117	1.114
	Berry	1.117	
	Inagaki	1.108	
	Kurata	0.340	
	Baumann	1.203	
H-TPIC	Stockmayer	1.183	1.200
	Berry	1.202	
	Inagaki	1.206	

a: The data of Kurata was excluded from the averages.

(IV) used A_2 values obtained from the osmotic measurements in toluene at 37°C. In case of method (V), the K_0 values for each series of fractions are obtained from the relation[25]

$$[\eta]_\theta = K_0 M^{1/2}.$$

Then the values of $(\langle R^2 \rangle_0 / M)^{1/2}$ corresponding to each fraction have been calculated from the K_0 values obtained, and are plotted against $M^{1/2}$ to yield parameter A.

The respective plots are shown in Fig. 11 to 15, the straight lines being an empirical best fit to the data. Also shown for comparison in Table V are the values of the parameters A estimated from the intercepts of the straight lines. Reasonably good agreement for the A values of the given polymer species was found except for the case of Kurata plot. This deviation was considered to be mainly due to the temperature at which the A_2 determined, 37°C instead of 25°C, and partly to the low sensitivity of A_2 to molecular weight. In any

case, however, the A values of n-PHIC appeared to be higher than that of p-PTIC or H-TPIC, suggesting the molecular stiffness of hexyl homoplymer.

A comparison of data on parameter A between p-PTIC and H-TPIC in Table V makes it certain that the unperturbed molecular dimension of copolymer containing 16 mole percent of tolyl content in toluene is almostly the same as that of tolyl homopolymer, even though the p-PTIC has marked a little lower values in its A value than copolymer. From this result and the reported value of reactivity ratio on H-TPIC[7], the molecular shape of H-TPIC in toluene at θ-condition was estimated as a interrupted helix structure with short blocks of n-hexyl isocyanate units.

Much effort was directed to the characterization of the polymers concerned. Future articles will present additional aspects of the polymer solubility parameters calculated

from the enthalpy parameter.

References

1. V.E. Shashoua, W.E. Sweeny & R.F. Tietz, *J. Am. Chem. Soc.*, **82**, 866 (1960).
2. W. Buchard, *Makromol., Chem.*, **67**, 182 (1963).
3. N.S. Schneider, S. Furusaki & R.W. Lenz, *J. Polymer Sci.*, A-3 933 (1965).
4. L.J. Fetters & H. Yu, *Macromolecules, 4*, 385 (1971).
5. M.R. Ambler, D. McIntyre & L.J. Fetters, *Macromolecules,* **11**, 300 (1978).
6. C.N. Tsvetkov, *Eur. Polym. J. Suppl.*, 237 (1969).
7. D.C. Lee, *J. Korean Chem. Soc.*, **17**, 371 (1973).
8. P.J. Flory, "Principles of polymer chemistry" Cornell Univ. Press., Ithaca, New York, p280, (1953).
9. M.L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1952).
10. D.F. Mead & R.M. Fuoss, *J. Am. Chem. Soc.*, **64**, 277 (1942).
11. A.R. Shultz & P.J. Flory, *J. Am. Chem. Soc.*, **74**, 4760 (1952), **75**, 3888 (1953).
12. P.J. Flory, "Principles of polymer chemistry" Cornell Univ. Press., Ithaca, New

York, p547 (1953).
13. P.J. Flory, *J. Chem. Phys.*, **18**, 1086 (1950).
14. B.H. Zimm, ibid, **14**, 164 (1946).
15. M.N. Berger, *J. Macromol. Sci. Revs. Macromol. Chem.*, C-9(2) 288 (1973).
16. L.J. Fetters & H. Yu, *Macromolecules*, **4**, 385 (1971).
17. M.N. Berger & B. M. Tidswell, IUPAC International Symposium on Macromolecules, Helsinki, 1972, Preprints II.
18. T.G. Fox, JR. & P.J. Flory, *J. Am. Chem. Soc.*, **73**, 1909 (1951).
19. H. Morawetz, "Macromolecules in Solution" 2nd edition, John Wiley & Sons Inc., p63 (1975).
20. A.R. Shultz & P.J. Flory, *J. Am. Chem. Soc.*, **74**, 4760 (1952).
21. R.W. Richards, *Polymer*, **18**, 114 (1977).
22. P.J. Flory, "Principles of Polymer Chemistry" Cornell Univ. Press., Ithaca, New York, p612 (1953).
23. H. Yamakawa, "Modern Theory of Polymer Solutions" Harper & Row, p364 (1971).
24. H. Yamakawa, ibid, p298 (1971).
25. H. Yamakawa, ibid, Chap. 7, (1971).
26. J.M.G. Cowie, *Polymer,* **7**, 487 (1966).
27. G.C. Berry, *J. Chem. Phys.*, **46**, 1338 (1967).
28. M. Kurata, M. Fukatsu, H. Sotobayashi & H. Yamakawa, *J. Chem. Phys.*, **41**, 139 (1964).
29. H.J. Baumann, *J. Polymer Sci.*, B-3 1069 (1965).