Dimensions of Vinylidene Chloride-Alkyl Acrylate Copolymers in Flory Theta Solvents

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The effects of the length of the pendant side chain on the dimensions of polymer molecules in solution have as yet not been fully elucidated. Recent studies by Chinai[1] et al. on poly(alkyl methacrylates) and by Manson[2] et al. on poly(vinyl alkyl ethers) have shown reversals of the polymer chain extension with an increase in side chain length, but no explanation of these reversals has been given. In the present study we determined the unperturbed dimensions of four copolymers of vinylidene chloride and alkyl acrylates in the hope of obtaining experimental material which might aid in clarifying how the dimensions of a polymer molecule in solution are affected by the length of its pendant side chain.

Experimental

Preparation of Copolymers.—For the purpose of the present study, we prepared four vinylidene chloride-alkyl acrylate copolymers. The alkyl acrylates chosen were ethyl acrylate, *n*-butyl acrylate, *n*-hexyl acrylate and *n*-octyl acrylate. Commercial materials of these alkyl acrylates were distilled and, after small amounts of hydroquinone had been added, stored in a nitrogen atmosphere. Immediately before use, they were washed with a dilute aqueous solution of sodium hydroxide and sodium carbonate to remove the hydroquinone added.

For the preparation of each copolymer the following recipe was used: 100 parts of monomers with the molar ratio of vinylidene chloride to alkyl acrylate being 85/15; 200 parts of 0.1 wt.% aqueous solution of methyl cellulose (Metocell. 100 c. p. s.); and lauryl peroxide 0.1 wt.% to monomers. The polymerization was carried out for 15 hr. at 50°C, with the yield ranging from 30 to 40% of charged monomers. The polymers produced were separated by filtration, dissolved immediately in ethyl methyl ketone, and then precipitated by an addition of excess methanol. The precipitate was isolated by filtration and dried in vacuo to a constant weight. The dry material was again dissolved in ethyl methyl ketone and fractionally precipitated at 30 to 40°C, using methanol as a nonsolvent. Both to check the distribution of two monomer units and to evaluate the average fundamental molecular weight, M_0, of the copolymer, the chlorine contents

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[1] S. N. Chinai et al., *J. Polymer Sci.*, **41**, 475 (1959).

[2] J. A. Manson et al., *Makromol. Chem.*, 37, 187 (1960).

TABLE I. REFRACTIVE INDEX INCREMENTS FOR COPOLYMERS IN METHYL ETHYL KETONE

Polymer	$\partial n/\partial c$ (λ=4358 Å, at room temperature)
Poly(vinylidene chloride co ethyl acrylate)	0.135
Poly(vinylidene chloride co *n*-butyl acrylate)	0.142
Poly(vinylidene chloride co *n*-hexyl acrylate)	0.130
Poly(vinylidene chloride co *n*-octyl acrylate)	0.130

of the resulting fractions were determined by using the Carius method.

Phase Equilibria.—After a number of preliminary experiments, we found that ethyl acetoacetate is a relevant theta solvent for poly(vinylidene chloride co ethyl acrylate) and that benzyl alcohol is relevant for the remaining copolymers. Given amounts of either of these solvents and a given copolymer were placed in a test tube, 0.8 cm. in diameter, 20 cm. long, and fitted with a ground glass stopper. After the polymer had been dissolved by heating 70 to 80°C for 2 hr., the test tube was immersed in a thermostated water bath. Phase separation occurred when the temperature of the bath was gradually lowered; the rate of cooling used was 0.1°C per min. The temperature at which the separation commenced, T_p, was determined visually with the reproducibility of ± 0.1°C. For each given fraction this temperature was determined as a function of the polymer concentration, and then the critical solution temperature, T_c, of the fraction was found from the maximum of the T_p vs. concentration curve so obtained. By repeating a similar procedure for other fractions with different molecular weights, data for T_c as a function of molecular weight were derived. The desired theta temperature, i. e., the value of T_p for infinite molecular weight, can be deiermined by treating these data in the manner described by Flory[3].

Light Scattering and Viscosity Measurements.—In this work, besides studying the four copolymers in their respective theta conditions, we also measured their dilute solution properties in ethyl methyl ketone for the sake of comparison.

The light-scattering behavior of given solutions was studied by means of a photometer of the Brice type manufactured by Shimadzu Seisakusho, Kyoto. Scattered intensities were measured at 45, 90 and 135°C to the incident beam, and the data obtained were analyzed in terms of the usual procedure[4], assuming a polydisperse random coil for the solute polymer molecule. Dust was removed from the test solutions by centrifugation at 20000 g. for 1.5 hr. Light-scattering measurements were carried out at room temperature. The refractive index increments of the ethyl methyl ketone solution of these copolymers were measured by a Debye-type differential refractometer manufactured by Shimadzu Seisakusho, Kyoto; the values obtained are listed in Table I. The viscosity measurements were performed at 30°C for ethyl methyl ketone solutions and at respective theta temperatures for ethyl acetoacetate or benzyl alcohol solutions.

The viscosities of ethyl methyl ketone solutions of the four copolymers were measured in an Ostwald viscometer; the flow time for ethyl methyl ketone at 30°C was 99.6 sec. Kinetic energy corrections were applied to the measured flow times. Use was made of Ubbelohde dilution viscometers for the study under theta conditions. These viscometers were designed so that their flow times for the theta solvents at the theta temperatures were relatively large; thus no kinetic energy correction was necessary.

Results and Discussion

Composition of Copolymers and Average Fundamental Molecular Weight M_0.—The chlorine contents of fractions of the four copolymers studied are listed in Tables II, III,

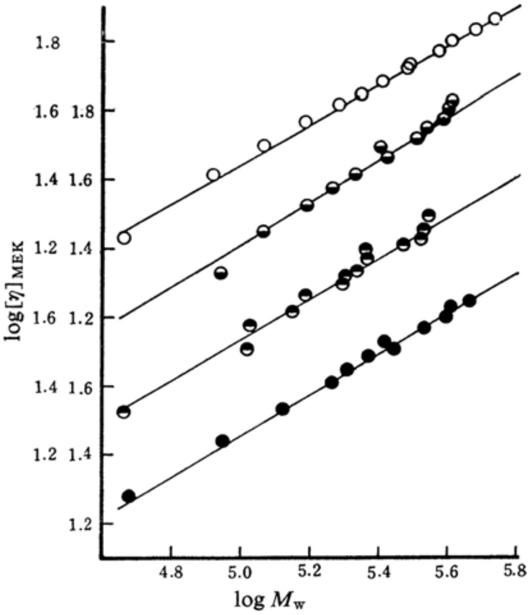

Fig. 1. Logarithmic plot of limiting viscosity number for fractions of copolymers in ethyl methyl ketone against molecular weight.

- ○ Poly(vinylidene chloride co *n*-octyl acrylate)
- ◒ Poly(vinylidene chloride co *n*-hexyl acrylate)
- ◓ Poly(vinylidene chloride co *n*-butyl acrylate)
- ● Poly(vinylidene chloride co ethyl acrylate)

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[3] P. J. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca (1953).

[4] P. Doty et al., *J. Chem. Phys.*, **18**, 1211 (1950).

TABLE II. LIGHT SCATTERING AND VISCOSITY DATA FOR POLY(VINYLIDENE CHLORIDE CO ETHYL ACRYLATE)

Fraction	Cl %	$[\eta]_{MEK}$ at 30°C 100 cc./g.	$[\eta]_{\theta}$ 100 cc./g.	$M_w \times 10^{-5}$	$\langle r^2 \rangle_w^{1/2} \times 10^6$ cm.	$\Phi \times 10^{-21}$
F-1	62.3	0.710	0.420	4.63	4.93	2.74
F-2	61.9	0.685	0.403	4.08	4.63	2.81
F-3	61.9	0.640	0.393	3.97	4.82	2.27
F-4	61.7	0.590	0.405	3.41	4.26	2.60
F-5	62.2	0.545	0.365	2.61	3.60	3.06
F-6	61.9	0.510	0.345	2.80	3.52	3.26
F-7	61.9	0.490	0.335	2.35	3.37	3.00
F-8	62.3	0.445	0.300	2.03	3.06	3.15
F-9	62.1	0.410	0.280	1.84	3.06	2.63
F-10	62.1	0.340	0.245	1.33	2.96	1.74
F-11	62.3	0.275	0.212	0.89	—	—
F-12	61.3	0.190	0.145	0.48	—	—
	av. 62.0					av. 2.73

TABLE III. LIGHT SCATTERING AND VISCOSITY DATA FOR POLY(VINYLIDENE CHLORIDE CO *n*-BUTYL ACRYLATE)

Fraction	Cl %	$[\eta]_{MEK}$ at 30°C 100 cc./g.	$[\eta]_{\theta}$ 100 cc./g.	$M_w \times 10^{-5}$	$\langle r^2 \rangle_w^{1/2} \times 10^6$ cm.	$\Phi \times 10^{-21}$
F-1	58.1	0.795	0.405	3.51	4.93	2.33
F-2	58.1	0.720	0.403	3.37	3.97	3.89
F-3	57.8	0.680	0.400	3.35	3.82	4.09
F-4	58.2	0.665	0.395	2.98	4.41	2.27
F-5	57.7	0.630	0.385	2.32	3.67	2.95
F-6	58.0	0.590	0.365	2.32	3.67	2.77
F-7	58.2	0.545	0.340	2.18	3.52	2.72
F-8	58.2	0.525	0.335	2.02	3.52	2.42
F-9	58.0	0.495	0.323	1.98	3.45	2.39
F-10	57.8	0.460	0.305	1.54	2.96	2.72
F-11	58.3	0.410	0.280	1.42	2.77	2.73
F-12	58.0	0.375	0.267	1.08	2.49	2.63
F-13	57.7	0.320	0.230	1.05	—	—
F-14	57.1	0.210	0.165	0.46	—	—
	av. 57.9					av. 2.83

TABLE IV. LIGHT SCATTERING AND VISCOSITY DATA FOR POLY(VINYLIDENE CHLORIDE CO *n*-HEXYL ACRYLATE)

Fraction	Cl %	$[\eta]_{MEK}$ at 30°C 100 cc./g.	$[\eta]_{\theta}$ 100 cc./g.	$M_w \times 10^{-5}$	$\langle r^2 \rangle_w^{1/2} \times 10^6$ cm.	$\Phi \times 10^{-21}$
F-1	57.2	0.685	0.365	4.08	4.71	2.68
F-2	57.3	0.655	0.350	4.02	4.26	3.40
F-3	57.7	0.610	0.333	3.86	4.11	3.38
F-4	57.6	0.575	0.325	3.48	3.97	3.21
F-5	57.7	0.535	0.310	3.23	3.67	3.49
F-6	58.0	0.505	0.302	2.54	3.52	2.93
F-7	57.6	0.470	0.290	2.66	3.52	2.86
F-8	57.5	0.420	0.268	2.16	3.37	2.36
F-9	57.3	0.380	0.240	1.84	3.37	1.82
F-10	57.8	0.340	0.218	1.55	3.06	1.84
F-11	56.8	0.285	0.185	1.16	2.68	1.72
F-12	57.4	0.215	0.140	0.88	—	—
	av. 57.5					av. 2.61

TABLE V. LIGHT SCATTERING AND VISCOSITY DATA FOR POLY(VINYLIDENE CHLORIDE CO n-OCTYL ACRYLATE)

Fraction	Cl %	$[\eta]_{MEK}$ at 30°C 100 cc./g.	$[\eta]_\theta$ 100 cc./g.	$M_w \times 10^{-5}$	$\langle r^2\rangle_w^{1/2} \times 10^6$ cm.	$\Phi \times 10^{-21}$
F-1	54.2	0.740	0.405	5.41	4.82	3.58
F-2	54.1	0.690	0.390	4.75	4.41	3.82
F-3	54.9	0.640	0.375	4.10	3.82	4.71
F-4	55.2	0.595	0.360	3.77	3.37	5.85
F-5	54.3	0.545	0.347	3.09	2.87	7.12
F-6	53.9	0.530	0.313	3.06	2.68	8.43
F-7	53.7	0.485	0.295	2.56	2.68	6.41
F-8	54.6	0.445	0.273	2.23	2.68	5.16
F-9	54.4	0.415	0.265	1.93	2.49	5.20
F-10	54.4	0.370	0.235	1.54	2.11	6.11
F-11	54.4	0.315	0.212	1.16	1.92	5.21
F-12	54.6	0.260	0.175	0.84	—	—
F-13	52.3	0.170	0.117	0.44	—	—
	av. 54.2					av. 5.14

TABLE VI. COMPOSITION AND FUNDAMENTAL MOLECULAR WEIGHT, M_0, OF COPOLYMERS

Polymer	Composition (mol. % of acrylate)	M_0
Poly(vinylidene chloride co ethyl acrylate)	14.9	97.5
Poly(vinylidene chloride co n-butyl acrylate)	16.7	102.2
Poly(vinylidene chloride co n-hexyl acrylate)	14.5	105.6
Poly(vinylidene chloride co n-octyl acrylate)	15.6	110.6

IV and V. Table VI gives the data for the composition and the fundamental average molecular weight, M_0, in each copolymer computed from these chlorine content values. The molar compositions of the four copolymers are not exactly the same, but the differences among them are small. Hence, if we take into consideration the experimental errors in determining the chlorine content, one may assume that these copolymers are uniform in molar composition.

Relation between Limiting Viscosity Number and Molecular Weight for Ethyl Methyl Ketone Solutions. — Tables II, III, IV and V list the limiting viscosity numbers of fractions of respective copolymers in ethyl methyl ketone at 30°C. and the weight-average molecular weights, M_w, of those fractions. Log-log plots for the limiting viscosity number against M_w prepared from these data are shown in Fig. 1 and yield the following relations:

Poly(vinyldene chloride co ethyl acrylate)

$$[\eta]_{MEK} = 2.88 \times 10^{-4} M_w^{0.60}$$

Poly(vinylidene chloride co n-butyl acrylate)

$$[\eta]_{MEK} = 3.43 \times 10^{-4} M_w^{0.60}$$

Poly(vinylidene chloride co n-hexyl acrylate)

$$[\eta]_{MEK} = 2.07 \times 10^{-4} M_w^{0.62}$$

Poly(vinylidene chloride co n-octyl acrylate)

$$[\eta]_{MEK} = 3.55 \times 10^{-4} M_w^{0.58}$$

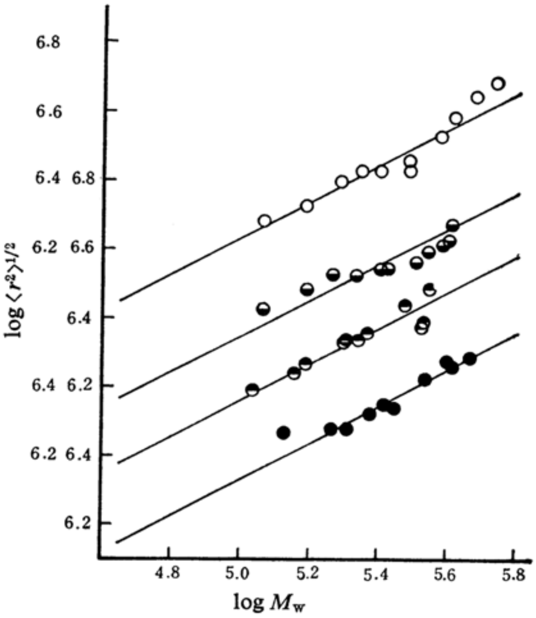

Fig. 2. Logarithmic plot for root mean square end-to-end distance of fractions of copolymers against molecular weight.

- ○ Poly(vinylidene chloride co n-octyl acrylate)
- ◒ Poly(vinylidene chloride co n-hexyl acrylate)
- ◓ Poly(vinylidene chloride co n-butyl acrylate)
- ● Poly(vinylidene chloride co ethyl acrylate)

It is interesting that the exponent to the weight-average molecular weight is almost identical for the four copolymers, suggesting that the chain flexibilities of these polymers are similar.

Relation between Molecular Dimension in Ethyl Methyl Ketone and Molecular Weight.— Tables II to V also contain values for the weight-average mean square end-to-end distance of the solute molecule, $\langle r^2\rangle_w^{1/2}$, evaluated from dissymmetry data. The log-log plots for $\langle r^2\rangle_w^{1/2}$ against M_w shown in Fig. 2 give the following relations:

Poly(vinylidene chloride co ethyl acrylate)

$$\langle r^2\rangle_w^{1/2}=4.90\times10^{-9}M_w^{0.53}$$

Poly(vinylidene chloride co *n*-butyl acrylate)

$$\langle r^2\rangle_w^{1/2}=5.29\times10^{-9}M_w^{0.53}$$

Poly(vinylidene chloride co *n*-hexyl acrylate)

$$\langle r^2\rangle_w^{1/2}=5.01\times10^{-9}M_w^{0.53}$$

Poly(vinylidene chloride co *n*-octyl acrylate)

$$\langle r^2\rangle_w^{1/2}=3.89\times10^{-9}M_w^{0.53}$$

In order to see the effect of length of the pendant side chain, it is convenient to write these relations in the form in which M_w is replaced by P_w, the weight-average degree of polymerization. The result is

Poly(vinylidene chloride co ethyl acrylate)

$$\langle r^2\rangle_w^{1/2}=5.55\times10^{-8}P_w^{0.53}$$

Poly(vinylidene chloride co *n*-butyl acrylate)

$$\langle r^2\rangle_w^{1/2}=6.14\times10^{-8}P_w^{0.53}$$

Poly(vinylidene chloride co *n*-hexyl acrylate)

$$\langle r^2\rangle_w^{1/2}=5.92\times10^{-8}P_w^{0.53}$$

Poly(vinylidene chloride co *n*-octyl acrylate)

$$\langle r^2\rangle_w^{1/2}=4.71\times10^{-8}P_w^{0.53}$$

The expressions indicate that the difference in the length of the pendant alkyl group has a relatively minor influence on the dimension of the vinylidene chloride-alkyl acrylate copolymer molecule in ethyl methyl ketone (a relatively good solvent for polymer) if the molar ratio of alkyl acrylate is as small as of the order of 0.15.

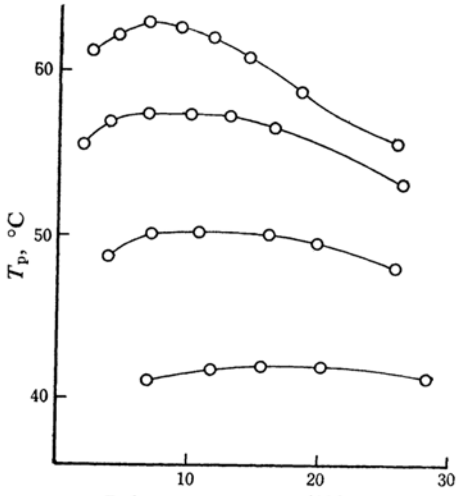

Fig. 3. Phase separation temperature, T_p, of four fractions of poly(vinylidene chloride co *n*-octyl acrylate) as a function of polymer concentration.

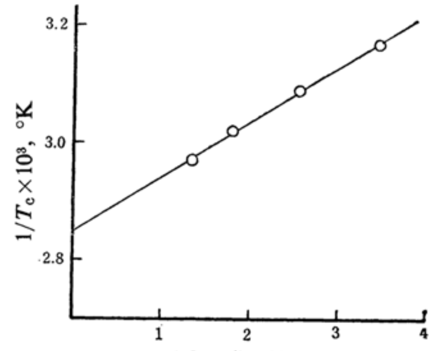

Fig. 4. Reciprocal critical solution temperature, T_c, against reciprocal square root of molecular weight of four fractions of poly(vinylidene chloride co *n*-octyl acrylate).

Theta Temperatures. — Figure 3 illustrates plots for T_p against the polymer concentration of poly(vinylidene chloride co *n*-octyl acrylate) in benzyl alcohol; the data for the other copolymers studied are similar in nature. From the maximum of each cure curve, the value of T_c for each fraction can be determined without ambiguity. According to the theory developed by Flory³⁾, T_c is related to the molecular weight M by the equation:

$$1/T_c=1/\theta(1+b/M^{1/2}) \qquad (1)$$

where b is a constant characteristic of a given polymer-solvent system. The so-called theta temperature θ, i. e., the critical solution temperature for a polymer of infinite chain length, can be determined by plotting $1/T_c$ against $1/M^{1/2}$ and then extrapolating the resulting plot to infiite molecular weight. Figure 4 shows this plot for poly(vinylidene chloride co *n*-octyl acrylate); similar linear plots were obtained for the remaining copolymers. The values of θ found in this way for poly (vinylidene chloride co *n*-butyl acrylate), poly (vinylidene chloride co *n*-hexyl acrylate), and poly(vinylidene chloride co *n*-octyl acrylate), all in benzyl alcohol, were 44.0, 56.8 and 77.9°C respectively, while that for poly(vinylidene

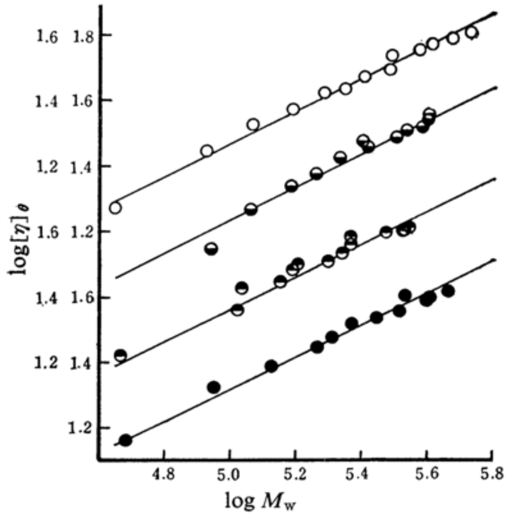

Fig. 5. Logarithmic plot for limiting viscosity number at θ temperature against molecular weight of fractions of copolymers.

○ Poly(vinylidene chloride co *n*-octyl acrylate)
◒ Poly(vinylidene chloride co *n*-hexyl acrylate)
◓ Poly(vinylidene chloride co *n*-butyl acrylate)
● Poly(vinylidene chloride co ethyl acrylate)

chloride co ethyl acrylate) in ethyl acetoacetate was 49.6°C.

Relation between Limiting Viscosity Number at Theta Temperature and Molecular Weight.—In Tables II to V are given the limiting viscosity numbers of fractions of the four copolymers in respective theta solvents. These values, $[\eta]_\theta$, are logarithmically plotted against M_w (determined above from light scattering data on ethyl methyl ketone solutions) in Fig. 5. The plots in the figure yield the following relations:

Poly(vinylidene chloride co ethyl acrylate)

$$[\eta]_\theta = 6.64 \times 10^{-4} M_w^{1/2}$$

(in ethyl acetoacetate)

Poly(vinylidene chloride co *n*-butyl acrylate)

$$[\eta]_\theta = 7.30 \times 10^{-4} M_w^{1/2}$$

(in benzyl alcohol)

Poly(vinylidene chlorride co *n*-hexyl acrylate)

$$[\eta]_\theta = 5.50 \times 10^{-4} M_w^{1/2}$$

(in benzyl alcohol)

Poly(vinylidene chloride co *n*-octyl acrylate)

$$[\eta]_\theta = 5.87 \times 10^{-4} M_w^{1/2}$$

(in benzyl alcohol)

In all case the values of $[\eta]_\theta$ increase in proportion to one half the power of M_w, in conformity with the current theories of dilute polymer solutions.

Dimensions of the Copolymers in Theta Solvents.—The values of the parameter Φ characterizing Flory's theory of dilute polymer solution have been calculated by substituting the data for $[\eta]$, $\langle r^2 \rangle_w^{1/2}$ and M_w obtained with ethyl methyl ketone solutions into the equations:

$$[\eta] = \boldsymbol{k}(M_w)^\alpha \quad (2)$$

$$K = \Phi \langle r^2 \rangle_w^3 / (M_w)^{3/2} \quad (3)$$

The results are shown in Tables II to V. It is seen that the Φ values so obtained for poly(vinylidene chloride co ethyl acrylate), poly(vinylidene chloride co *n*-buthyl acrylate), and poly(vinylidene chloride co *n*-hexyl acrylate) agree fairly well with each other and are not very different from the generally accepted value, 2.1×10^{-21}. However, the values for poly(vinylidene chloride co *n*-octyl acrylate) are unusually high. The reason for this is not clear to us but is probably due to the experimental errors involved in $\langle r^2 \rangle_w$.

Equations 2 and 3 may be used to calculate the weight-average root mean square end-to-end distance, $\langle r_0^2 \rangle_w^{1/2}$, of the polymer molecule in the theta solvent from the measured values of $[\eta]_\theta$ and M_w if the value of the parameter Φ is given, since α is equal to 1/2 under theta conditions. We have made this calculation, assuming $\Phi = 2.1 \times 10^{-21}$, for all the copolymers studied here. The results are:

Poly(vinylidene chloride co ethyl acrylate)

$$\langle r_0^2 \rangle_w^{1/2} = 6.81 \times 10^{-9} M_w^{1/2} \quad (49.6°\text{C})$$

Poly(vinylidene chloride co *n*-butyl acrylate)

$$\langle r_0^2 \rangle_w^{1/2} = 7.03 \times 10^{-9} M_w^{1/2} \quad (44.0°\text{C})$$

Poly(vinylidene chloride co *n*-hexyl acrylate)

$$\langle r_0^2 \rangle_w^{1/2} = 6.04 \times 10^{-9} M_w^{1/2} \quad (56.8°\text{C})$$

Poly(vinylidene chloride co *n*-octyl acrylate)

$$\langle r_0^2 \rangle_w^{1/2} = 6.53 \times 10^{-9} M_w^{1/2} \quad (77.9°\text{C})$$

In terms of P_w these relations may be written:

Poly(vinylidene chloride co ethyl acrylate)

$$\langle r_0^2 \rangle_w^{1/2} = 6.72 \times 10^{-8} P_w^{1/2} \quad (49.6°\text{C})$$

Poly(vinylidene chloride co *n*-butyl acrylate)

$$\langle r_0^2 \rangle_w^{1/2} = 7.11 \times 10^{-8} P_w^{1/2} \quad (44.0°\text{C})$$

Poly(vinylidene chloride co *n*-hexyl acrylate)

$$\langle r_0^2 \rangle_w^{1/2} = 6.58 \times 10^{-8} P_w^{1/2} \quad (56.8°\text{C})$$

Poly(vinylidene chloride co *n*-octyl acrylate)

$$\langle r_0^2 \rangle_w^{1/2} = 6.87 \times 10^{-8} P_w^{1/2} \quad (77.9°\text{C})$$

TABLE VII. COMPARISON OF UNPERTURBED MOLECULAR PARAMETERS ON VARIOUS POLYMERS

Polymer	θ °C	$(\langle r_0^2\rangle/P)^{1/2}$ $\times 10^8$	$(\langle r_0^2\rangle/$ $\langle r_{0f}^2\rangle)^{1/2}$	$M_0[\eta]_\theta/$ $P^{1/2}$	Ref.
Poly(vinylidene chloride co ethyl acrylate)	49.6	6.72	2.18	0.63	
Poly(vinylidene chloride co *n*-butyl acrylate)	44.0	7.11	2.31	0.74	
Poly(vinylidene chloride co *n*-hexyl acrylate)	56.8	6.58	2.14	0.61	
Poly(vinylidene chloride co *n*-octyl acrylate)	77.9	6.87	2.23	0.68	
Poly(methyl methacrylate)	25.0	4.88	2.24	0.59	1
Poly(ethyl methacrylate)	23.0	4.20	1.94	0.57	1
Poly(*n*-butyl methacrylate)	21.5	4.52	2.09	0.50	1
Poly(*n*-hexyl methacrylate)	32.6	5.33	2.44	0.95	1
Poly(*n*-octyl methacrylate)	16.8	4.99	2.32	0.75	1
Poly(*n*-lauryl methacrylate)	13.0	7.80	3.58	1.30	1
Poly(styrene)	25.0	6.81	2.14	0.89	5
Poly(isobutylene)	24.0	5.95	1.93	0.45	6
Poly(vinyl acetate)	26.5	7.01	2.28	0.73	7
Poly(cyclohexyl methacrylate)	23.0	7.05	2.29	0.73	8
Poly(vinyl benzoate)	32.5	8.15	2.65	1.14	9

The quantity $(\langle r_0^2\rangle_w/P_w)^{1/2}$ provides a measure of the extension of a polymer chain, and it is seen that the values of this quantity for all four copolymers are almost the same. If we take into account the fact that the unperturbed dimension of a polymer molecule may decrease with increasing temperature (due to the enhanced rotation of each chain element), it is likely that, when a comparison is made at a fixed temperature, the values of this quantity for the four copolymers will become closer. We can therefore conclude that if the molar ratio of alkyl acrylate component is relatively small, the unperturbed dimension of vinylidene chloride-acrylate copolymer is hardly affected by the length of the pendant alkyl group.

Table VII summarizes the values of some basic parameters characterizing chain dimensions, such as $(\langle r_0^2\rangle/P)^{1/2}$, $(\langle r_0^2\rangle/\langle r_{0f}^2\rangle)^{1/2}$, and $M_0\ [\eta]_\theta/P^{1/2}$, for the four copolymers studied here, together with those for several other polymers[1,5-9]. Here $\langle r_{0f}^2\rangle^{1/2}$ denotes the root mean square end-to-end distance in the unperturbed state of a polymer molecule in which no hindrance to the rotation of each element is present. Its value has been calculated assuming a value of 1.54Å for the distance between neighboring carbon atoms and a value of 109.5° for the valency angle between successive bonds. The parameter $M_0\ [\eta]_\theta/P^{1/2}$ has been proposed by Chinai and associates.

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