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Dilute Solution Properties of Polystyrene, Polymethyl Methacrylate, and Their Random Copolymers

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ABSTRACT

Intrinsic viscosities of polystyrenes (PS), polymethyl methacrylates (PMMA), and their random copolymers have been determined at different temperatures to estimate chain flexibility of homopolymers and copolymers. The coefficients K_e , the chain flexibility descriptor, for PS decreases with increasing M_n and have positive values. For PMMA the K_e increase slightly with increasing M_n and have negative values. The K_e values for S/MMA copolymers are all positive, showing that the chain flexibility in copolymers is predominantly influenced by styrene concentration. For PS the long-range parameter B and the excluded volume factor Z increase from 25 to 45°C and thereafter remain constant. The short-range parameter, A, for PS remains virtually unchanged with the change in temperature. For PMMA, the short-range, the long-range, and the excluded volume factors remain virtually constant between 25 and 65°C.

INTRODUCTION

A number of workers [1-3] have recently investigated the viscosity-temperature relationship for various homopolymers with a

view to characterizing chain flexibility. The viscosity of dilute polymer solutions varies with temperature according to Arrhenius-type law,

$$\eta = A \exp \frac{Q}{RT} \quad (1)$$

where η is the viscosity of solutions, Q the apparent activation energy of viscous flow, and A the preexponential factor. Activation energy (Q) and preexponential factor (A) are both related to molecular weight and concentration.

The apparent activation energy (Q) can also be related to the flexibility or stiffness of polymer chains in dilute solutions,

$$Q = Q_0 + K_e MC \quad (2)$$

where Q_0 is a constant dependent on the solvent, the coefficient K_e depends both on the nature of the solvent and of the polymer, and M and C are the molecular weight of the polymer and concentration of solution, respectively. The value of K_e is descriptive of chain flexibility. The coefficient K_e also influences the short-range, the long-range parameters, and the volume expansion factor of polymer chains in solution.

The dimensions of polymer chains in solution are greatly influenced by interactions between chain elements. These interactions are conveniently divided into two classes. The short-range interactions are those between atoms or groups separated by only a small number of valence bonds. They result in the effective constancy of bond angles and the torque hindering internal rotations. The long-range interactions, on the other hand, are those between nonbonded groups which are separated in the basic chain structure by many valence bonds. They are therefore similar in nature and magnitude to van der Waals' interactions between the parts of two different molecules. The long-range interactions give rise to the so-called "excluded volume effect" which can be pictured as an osmotic swelling of the randomly coiled chain by the solvent-polymer interactions. This effect vanishes under a special condition of temperature or solvent which is usually known as the "theta" temperature or solvent. For most polymers the theta condition can rarely be obtained at ordinary temperatures so that short-range interaction can be estimated without the perturbations of the long-range interactions. The viscosities of dilute polymer solutions provide the main experimental information on chain dimensions but their interpretation demands a separation of the effects of the two types of interaction from each other. A number of equations have been proposed for this purpose and an excellent review has been

presented by Kurata and Stockmayer [9]. These are all semi-empirical refinements of Flory excluded volume theory and the Flory-Fox viscosity theory [13, 14].

In this study the coefficient K_e is related to the chain flexibility of homopolymers [polystyrene and poly(methyl methacrylate)] and compared to that of the random copolymers. The influence of temperature on the long- and short-range parameters and the excluded volume factor has been studied for polystyrene and poly(methyl methacrylate).

EXPERIMENTAL

Materials

Poly(methyl Methacrylate) (PMMA)

The PMMA samples were obtained from Scientific Polymer Products, Ontario, New York. Their weight- and number-average molecular weight, as determined by gel permeation chromatography, were as follows: (1) M_w , 33,111; M_n , 14,898; (2) M_w , 96,018; M_n , 50,009; (3) M_w , 563,334; M_n , 147,857.

Polystyrene (PS)

The PS samples were obtained from Pressure Chemical Co., Pittsburgh, Pennsylvania. The dispersity of these samples is less than 1.1 and therefore the M_n values are about the same as the M_w values: (1) M_w , 2000; (2) M_w , 4000; (3) M_w , 33,000; (4) M_w , 39,200; (5) M_w , 110,000; (6) M_w , 233,000.

Styrene-Methyl Methacrylate Copolymers (S/MMA)

The random copolymers were obtained by suspension polymerization. The composition was determined by pyrolysis gas chromatography and proton magnetic resonance spectrometry [4]. The number- and weight-average molecular weights were determined by gel permeation chromatography: (1) S/MMA, 85/15; M_w , 38,890; M_n , 21,605; (2) S/MMA, 50/50; M_w , 43,307; M_n , 23,940; (3) S/MMA, 15/85; M_w , 58,485; M_n , 30,941.

Viscosity Determinations

Viscosities of pure solvents and solution in the concentration range of 0.25 to 2.0 g/dL were measured at 25, 35, and 45°C in toluene (Eastman). Cannon-Ubbelohde type capillary viscometers were used.

TABLE 1. Molecular Weights and Activation Energy Coefficients for Polystyrene

Material	\bar{M}_w	\bar{M}_n	k_e	K_e
PS-1	2,000	2,000	57.6	2.88×10^{-2}
PS-2	4,000	4,000	80.8	2.02×10^{-2}
PS-3	33,000	33,000	98.34	2.98×10^{-3}
PS-4	39,200	20,000	134.0	6.7×10^{-3}
PS-5	110,000	110,000	16.5	1.5×10^{-4}
PS-6	233,000	233,000	7.46	3.2×10^{-5}

The viscometer constants ranged from 0.001186 to 0.03083. Measurements were made in a thermostatically controlled bath maintained at $\pm 0.01^\circ\text{C}$ of any temperature. All solvents and solutions were filtered before use.

RESULTS AND DISCUSSION

The coefficients K_e obtained for polystyrene, poly(methyl methacrylate), and their random copolymers are presented in Tables 1, 2, and 3. The coefficient K_e for polystyrene decreases with increasing molecular weight. This is shown as a log-log plot of K_e vs M_n in Fig. 1. There appears to be a change in slope around $M_n = 25,000$ which can be related to chain entanglement [5]. In poly(methyl methacrylate), K_e increases with increasing M_n (Fig. 2). The value of K_e 6.36×10^{-4} is in agreement with the one reported (K_e 6.1×10^{-4}) by Fort, Hutchinson, Moore, and Murphy [2]. However, the increase of K_e with molecular weight is less significant here than the decrease shown for polystyrene in Fig. 1. Also, the K_e values for polystyrene are positive compared to the negative values for poly(methyl methacrylate). This has been attributed to chain flexibility. The polystyrene chain is rigid compared to the relatively flexible chains of poly(methyl methacrylate). The K_e values as a function of styrene monomer in the copolymers is shown in Fig. 3. It can be seen that the K_e values are all positive and show a significant increase in value at 85% styrene concentration. It can be concluded that the rigidity of these copolymers is predominantly influenced by styrene and only a

TABLE 2. Molecular Weights and Activation Energy Coefficients for Poly(methyl methacrylate)

Material	\bar{M}_w	\bar{M}_n	k_e	K_e
PMMA-1	33,111	14,898	-9.475	-6.36×10^{-4}
PMMA-2	96,018	50,009	-23.004	-4.6×10^{-4}
PMMA-3	563,334	147,857	-47.906	-3.24×10^{-4}

TABLE 3. Molecular Weights and Activation Energy Coefficients for Styrene Methyl Methacrylate Copolymers

Material	Composition	\bar{M}_w	\bar{M}_n	k_e	K_e
$\left\{ \frac{S}{MMA} \right\}_n$	S/MMA 85/15	38,890	21,605	23.982	1.3×10^{-3}
$\left\{ \frac{S}{MMA} \right\}_n$	50/50	43,307	23,940	26.573	1.1×10^{-3}
$\left\{ \frac{S}{MMA} \right\}_n$	15/85	58,458	30,941	43.317	1.4×10^{-3}

small concentration of methyl methacrylate increases the flexibility in copolymers.

Kotaka, Murakami, and Inagaki [6] determined short-range and long-range interaction parameters for styrene-methyl methacrylate copolymers in various solvents and their dependence on monomer composition. We have here studied the temperature dependence of these parameters on the two homopolymers. A recent study by one of the authors [7] shows agreement with the results of Kotaka et al. [6] on the influence of styrene concentration on the long-range parameter, B.

The intrinsic viscosity and the long-range parameter decrease with increasing temperature according to the Stockmayer-Fixman [8] equation,

$$[\eta]/M^{1/2} = K + 1.55\Phi_0'BM^{1/2} \quad (3)$$

where $[\eta]$ is the intrinsic viscosity, M is the molecular weight, K is the Mark-Houwink constant, and Φ_0' is a constant dependent on the homopolymer- θ solvent interaction and the long-range parameter. The short-range parameter A can be related by

$$K_0^{2/3} = \Phi_0^{2/3} A^2 \quad (4)$$

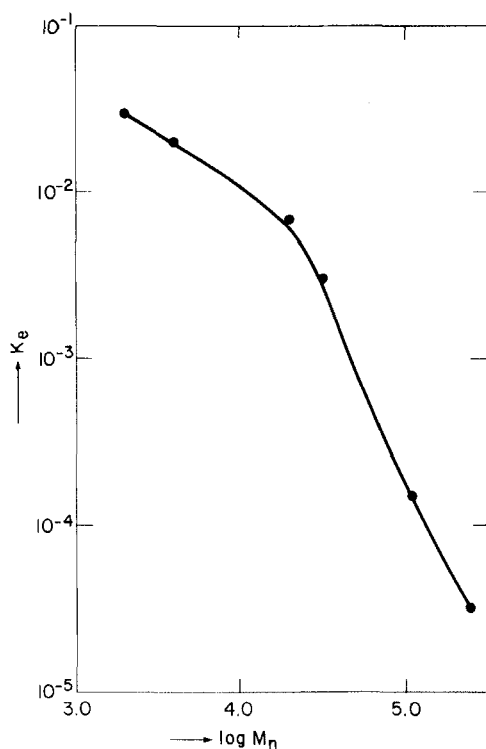


FIG. 1. Activation energy constant K_e and molecular weight of polystyrene.

where K_0 is a constant and Φ_0 is a viscosity parameter value (2.87×10^{21} in cgs units).

Kurata and Stockmayer [9] have proposed another relationship to determine the long-range parameter:

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + 0.363 \Phi_0 B [g(\alpha_\eta) M^{2/3}/(\eta)^{1/3}] \quad (5)$$

where $g(\alpha_\eta)$ is a coefficient dependent on α_η , the expansion factor.

Other constants and parameters in Eq. (5) have been defined earlier.

The main weakness of Eq. (3) is that at higher molecular weights $M^{1/2}$ is not linearly related to $\Phi_0 M^{1/2}$ [10]. We have therefore selected Eq. (5) to show the temperature dependence of short- and long-range parameters for polystyrene and poly(methyl methacrylate) in toluene. The $g(\alpha_\eta)$ for Eq. (5) is obtained from the following series of equations:

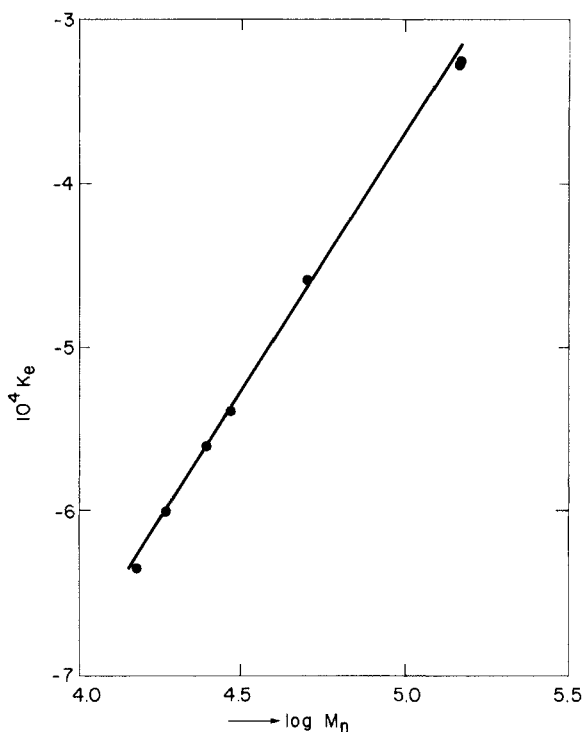


FIG. 2. Activation energy constant K_e and molecular weight of poly(methyl methacrylate).

$$[\eta]_{\theta} = KM^{1/2} \quad (6)$$

$$\alpha_{\eta} = \left[\frac{[\eta]}{[\eta]_{\theta}} \right]^{1/3} \quad (7)$$

$$g(\alpha_{\eta}) = 8\alpha_{\eta}^3 / (3\alpha_{\eta}^2 + 1)^{3/2} \quad (8)$$

Thus, by measuring $[\eta]$ for samples of known molecular weight, K and $g(\alpha_{\eta})$ can be determined. The well-known Mark-Houwink equation relates $[\eta]$ to the molecular weight:

$$[\eta] = KM^a \quad (9)$$

where K and a are constants.

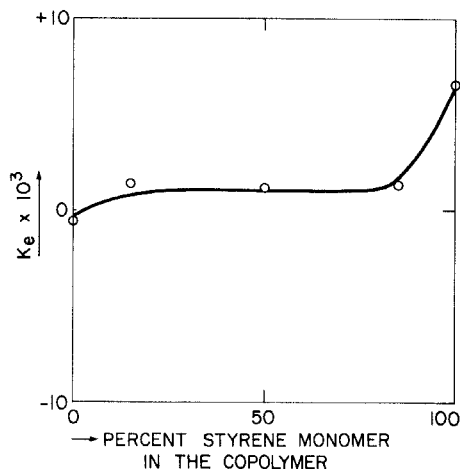


FIG. 3. Activation energy constant K_e and concentration of styrene in styrene/methyl methacrylate copolymer.

The excluded volume factor or the expansion factor Z is related to both the short- and long-range parameters:

$$Z = \left(\frac{B}{A^3} \right) M^{1/2} \quad (10)$$

The Mark-Houwink constant K , the short-range parameter A , the long-range parameter B , the volume expansion factor α_η , and the excluded volume factor Z for polystyrene and polymethyl methacrylate at different temperatures are provided in Tables 4 and 5.

The Mark-Houwink constant K decreases with increasing temperature for polystyrene [11] whereas it remains basically constant for poly(methyl methacrylate). The long-range parameter B increases with an increase in temperature for polystyrenes from 25 to 45°C and thereafter remains constant on further increases in temperature. On the other hand, the short-range parameter decreases slightly with an increase in temperature from 25 to 45°C and then remains constant on further increases in temperature. For poly(methyl methacrylate) both the short- and long-range parameters remain virtually constant with increases in temperature. As expected, the excluded volume factor Z increases for polystyrene with increasing temperature [12] from 25 to 45°C and then remains constant (Fig. 4). However, for poly(methyl methacrylate) this factor remains basically constant from 25 to 65°C (Fig. 5). The excluded volume factor is a linear

TABLE 4. Mark-Houwink Constant (K_0), Long Range (B), and Short Range (A) Parameters

Material	Temperature (°C)	Mark-Houwink constant (K)	Long range (B)	Short range (A)
Polystyrene	25	$(8.0 \times 10^{-4})^a$	$(107 \times 10^{-30})^a$	$(7.0 \times 10^{-9})^a$
	25	6.7×10^{-4}	121×10^{-30}	6.1×10^{-9}
	45	2.8×10^{-4}	278×10^{-30}	4.6×10^{-9}
	65	3.1×10^{-4}	263×10^{-30}	4.8×10^{-9}
Polymethyl methacrylate		$(5.0 \times 10^{-4})^a$	$(60 \times 10^{-30})^a$	$(2.3 \times 10^{-9})^a$
	25	2.7×10^{-4}	39.0×10^{-30}	4.5×10^{-9}
	45	2.4×10^{-4}	38.2×10^{-30}	4.4×10^{-9}
	65	2.3×10^{-4}	35.8×10^{-30}	4.3×10^{-9}

^aThese are the published values from Kotaka et al. [6]. Note the differences in PMMA between published and our values in K_0 , B and A are due to polydispersity in our samples, known in the literature.

TABLE 5. Volume Expansion Factor (α_η) and Excluded Volume Factor (Z) at 25°C

Material	\bar{M}_w	α_η^3	Z
Polystyrene	2,000	2.41	2.4×10^{-2}
	4,000	2.20	3.3×10^{-2}
	33,000	3.05	9.6×10^{-2}
	110,000	4.41	17.6×10^{-2}
	230,000	1.76	25.6×10^{-2}
Polymethyl methacrylate	33,000	2.35	7.4×10^{-2}
	96,000	2.68	12.7×10^{-2}
	563,000	3.80	30.8×10^{-2}

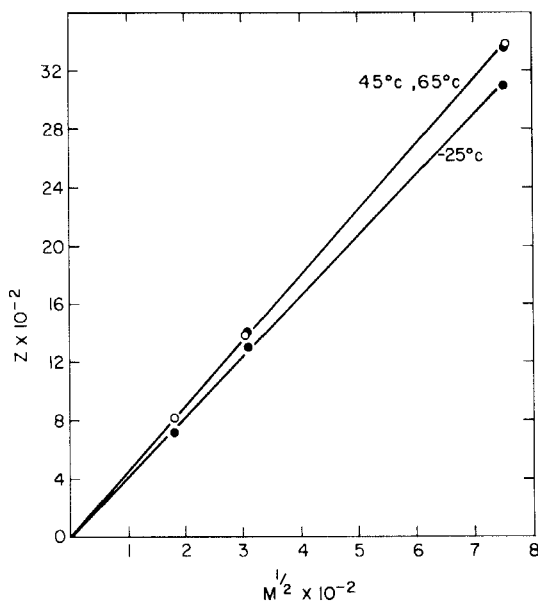


FIG. 4. Excluded volume Z and molecular weight of polystyrene.

function of molecular weight for both polystyrene and poly(methyl methacrylate) at the three temperatures as shown in Figs. 4 and 5.

The expansion factor α_η takes into consideration the non-Gaussian character of the chains due to the excluded volume. For PS the average value of this factor is 1.44 and for PMMA 1.43. Beccera, Radic, and Gargallo [15] have shown for various methacrylate derivatives in benzene that this factor is influenced by the substituents. For poly(pentachlorophenyl methacrylate) they have demonstrated that the factor is also influenced by the solvent. Yamakawa [12] discusses in detail the problem of relation α_η^3 and Z .

Berry [16] has reported values for α_η^3 and Z in toluene. He relates Z to the thermodynamic parameter β and the radius of gyration $\langle s_0^2 \rangle$ obtained from the light-scattering measurements according to

$$Z = \beta (\langle s_0^2 \rangle / M)^{-3/2} M^{1/2} \quad (11)$$

where M is the molecular weight and β is assumed to have a temperature dependence,

$$\beta = \beta_0 (1 - \theta / T) \quad (12)$$

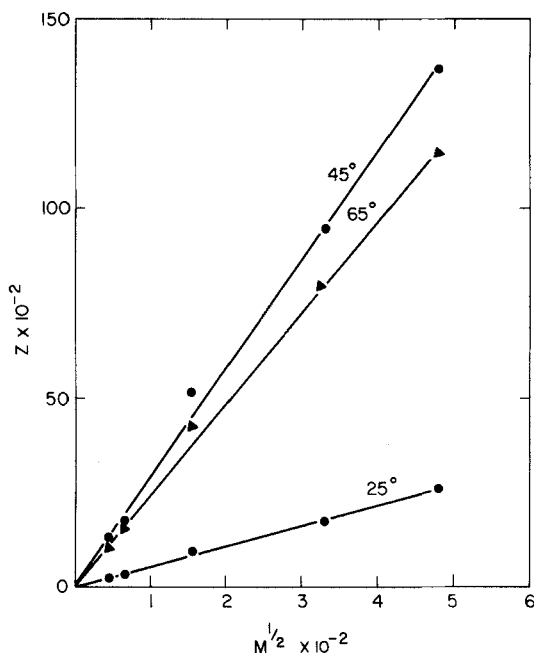


FIG. 5. Excluded volume Z and molecular weight of poly(methyl methacrylate).

where β_0 is a constant, θ is the theta temperature, and T is the temperature of measurement. Berry contends that α_η^3 is not a single-valued function of Z except for $M > \sim 10^6$ and that at lower molecular weights partial draining effects play a significant role. Our results (Table 5) have been obtained in a very narrow range of Z and the parameter Z itself has been calculated using the viscosity data vs Berry's light-scattering method. It is therefore difficult to make a valid comparison of the two sets of data. The parameter Z is not directly measurable, and it is recognized that the two parameter theories [12] along with the theory of equilibrium [12] have not provided a satisfactory solution to the theoretical basis of relating α_η^3 to Z .

In summary, the nature of homopolymer components and their influence on the chain flexibility of copolymers have been studied via the coefficient K_e . It is found that a relatively small concentration of styrene in PS/MMA copolymer has great influence on the chain flexibility of the copolymer. The K_e value for PS of 33,000 M_n is $\sim 3 \times 10^{-3}$ and that of PMMA is $\sim 4 \times 10^{-4}$. The K_e value of 15/85 S/MMA

copolymer of 31,000 M_n , however, is 1.4×10^{-3} . In other words, only 15% styrene in the copolymer introduces considerable rigidity to the polymer chain. Also, for a rigid chain like polystyrene, only the long-range parameter B and the excluded volume parameter Z can be influenced by temperature (between 25 and 45°C). These parameters are not influenced with further increases in temperature. For a flexible chain like PMMA, the short-range, the long-range, and the excluded volume factors are not influenced within the range of temperatures studied.

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