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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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To cite this Article Madruga, E. L. , Román, J. San and Guzmán, J.(1979) 'Radical Copolymerization of Acrylic Monomers. I. Effect of Solvent on the Copolymerization of Methyl Methacrylate and 1-Naphthyl Methacrylate', Journal of Macromolecular Science, Part A, 13: 8, 1089 – 1104

To link to this Article: DOI: 10.1080/00222337908056702

URL: <http://dx.doi.org/10.1080/00222337908056702>

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Radical Copolymerization of Acrylic Monomers. I. Effect of Solvent on the Copolymerization of Methyl Methacrylate and 1-Naphthyl Methacrylate

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ABSTRACT

A study of the radical copolymerization of methyl methacrylate and 1-naphthyl methacrylate in benzene, chlorobenzene, and o-dichlorobenzene was made at 50°C. There is a marked effect of solvent on both r_1 and r_2 in all these systems, which can be correlated with the variation in the polarity of solvents. The glass transition temperatures of copolymers were discussed taking into consideration the sequence distribution of the copolymers and the homopolymers t_g - values.

INTRODUCTION

It is clear from a number of recent papers [1-10] that solvents affect the reactivity ratios in free-radical copolymerization. The effect of the solvent on the reactivity ratios was first shown in 1969 by Ito and Otsu [1] for the radical copolymerization of methyl methacrylate and styrene. A great number of papers describe the radical copolymerization of monomers with opposite polarities; in this way,

styrene as the donor monomer has been copolymerized with methyl methacrylate [5], methacrylonitrile [11], and acrylonitrile [12] as acceptor monomers.

In a similar way, the effect of solvents in radical copolymerization of monomers with the same polarity has been pointed out; to date these papers have been scarce [2, 3, 10, 13-17].

The polymer glass transition is one of the most important phenomena in polymers. As is well known, the copolymer glass transition hardly changes with the composition of macromolecular chains. In order to explain the influence of the whole composition and the sequence distribution in statistical copolymers over the glass transition temperature, a great number of theories have been developed [18].

In the present paper the effect of solvents on the reactivity ratios for the pair methyl methacrylate-1-naphthyl methacrylate (both acceptor monomers) has been studied. The influence of the sequence distribution on the copolymer glass transition temperature has also been determined in the light of different theories.

EXPERIMENTAL

Monomers

1-Naphthyl methacrylate (A) was prepared by the reaction of methacryloyl chloride with 1-naphthol in 8-10% aqueous sodium hydroxide solution cooled in an ice bath according to the method developed by Patai [19]. The monomer was redistilled at 125-128°C/2 Torr; yield 75%.

ANALYSIS. Calculated for $C_{14}H_{12}O_2$: C, 79.22%; H, 5.69%. Found, C, 79.20%; H, 5.75%.

Methyl methacrylate was purified by conventional methods.

Initiator

The initiator, 2,2'-azobisisobutyronitrile (AIBN) (Fluka A. G.) was purified by fractional crystallization in methyl alcohol; mp = 104 ± 1°C.

Solvents

Acetone, benzene, chlorobenzene, and o-dichlorobenzene were purified by appropriate chemical methods [20]. The solvents were freshly distilled immediately prior to use.

Copolymerization

All experiments were performed in glass ampoules covered by aluminum foil. Copolymerizations were conducted at $50 \pm 0.1^\circ\text{C}$ under high vacuum. The required volumes of solvent, initiator, and monomers were added to the glass ampoules, and the mixture was degassed by successive freeze-pump-thaw cycles. Monomer and initiator concentrations were 3 mole/liter and 0.3 mole % of the total monomer concentration, respectively. Polymers conversion were kept lower than 10 weight %.

The resulting copolymers were isolated by pouring the contents of the glass ampoules into methanol containing hydroquinone. The precipitated materials were purified by reprecipitation from the benzene-methanol system and then filtered and dried under vacuum at 50°C until constant weight was attained.

Copolymer Analysis

Copolymer compositions were calculated by UV spectroscopy by using an UV-Vis Varian 350 spectrophotometer with 10^{-3} g/cc chloroform copolymer solutions. Previously a master curve was obtained with mixtures of homopolymer solutions in different compositions.

$^1\text{H-NMR}$ spectroscopy was also used to determine the copolymer compositions. The spectra were obtained at 60°C for all copolymers on about 8% solutions in deuteriochloroform by using a Varian XL-100 spectrometer. Hexamethyldisiloxane was used as internal standard reference.

Differential Scanning Calorimetry (DSC)

Glass transition temperatures have been measured with a Perkin-Elmer differential scanning calorimeter, model DSC-1B, which was calibrated with standard materials. Measurements as well as calibration were carried out at heating rates of 8 and $16^\circ\text{C}/\text{min}$. The differences in T_g values obtained at the two heating rates are less than 1°C .

RESULTS AND DISCUSSION

The analytical data for the copolymers used for the determination of reactivity ratios r_A and r_B by the Fineman-Ross method are shown

TABLE 1. Analytical Data for Copolymerization of 1-Naphthyl Methacrylate (A) and Methyl Methacrylate (B) in Different Solvents

Solvent	F _A (feed) (mole %)	F _B (copolymer) (mole %)	Conversion (weight %)
Benzene	0.200	0.247	10.02
Benzene	0.300	0.370	9.08
Benzene	0.400	0.510	9.90
Benzene	0.500	0.650	10.25
Benzene	0.600	0.680	9.34
Chlorobenzene	0.200	0.235	9.10
Chlorobenzene	0.300	0.383	9.35
Chlorobenzene	0.400	0.492	9.05
Chlorobenzene	0.500	0.605	10.00
Chlorobenzene	0.600	0.678	9.50
o-Dichlorobenzene	0.200	0.270	9.80
o-Dichlorobenzene	0.300	0.390	9.25
o-Dichlorobenzene	0.400	0.540	10.05
o-Dichlorobenzene	0.500	0.675	9.75
o-Dichlorobenzene	0.700	0.830	9.40

in Table 1, and the corresponding plots are shown in Figs. 1, 2 and 3. The values of r_A and r_B are quoted in Table 2; the errors were derived from the standard deviations in the slopes and intercepts of the straight lines obtained by the Fineman-Ross method (Figs. 1, 2, 3).

Kinetic anomalies do not seem to be evident in the composition range studied. The monomer feed composition practically does not change either during the copolymerization time for each of the solvents used, although from the data of Table I it is evident that all the solvents used in the copolymerization experiments affect to the copolymer composition considerably.

Both reactivity ratios change with the solvents, but the observed variation is higher for r_A . A solvent effect on the reactivity ratios implies a change in the ratio K_{ii}/K_{ij} , where K_{ii} and K_{ij} are the rate

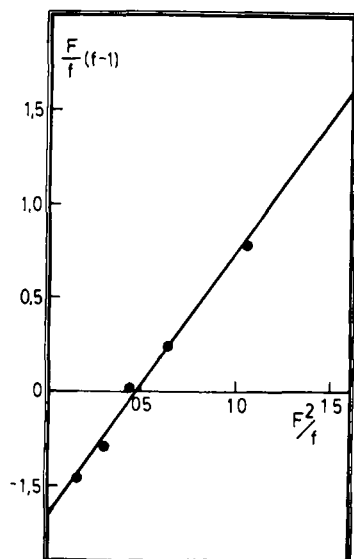


FIG. 1. Fineman-Ross plot of composition results from copolymerization of 1-naphthyl methacrylate and methyl methacrylate in benzene.

coefficients for the addition of *i* and *j* monomers, respectively, to growing *i* radicals. The increase of the reactivity ratios could be due to an increase of K_{ii} and/or decrease of K_{ij} . Variations in the propagation rate constants for the homopolymerization of the donor monomer styrene [21-24] and methyl methacrylate [25-28] in several solvents have been described. Often, the effect of solvents shows an opposite trend for the two monomers corresponding a decrease of K_p for styrene polymerizations to an increase of K_p for methyl methacrylate.

Bamford et al. [27] and later Cameron et al. [29] interpreted such results in terms of stability of the complex between growing radicals and solvent as compared to the reactivity of the growing chain towards the monomer. This interpretation can be considered as an extension of the well known radical complex theory developed by Henrici-Olivé and Olivé [21-23]. In a more general sense, it has been stated that "complexing" of the polymer growing radical can be regarded as an enhanced form of radical solvation by monomer and/or solvent.

In the present paper both monomers have acceptor character, and

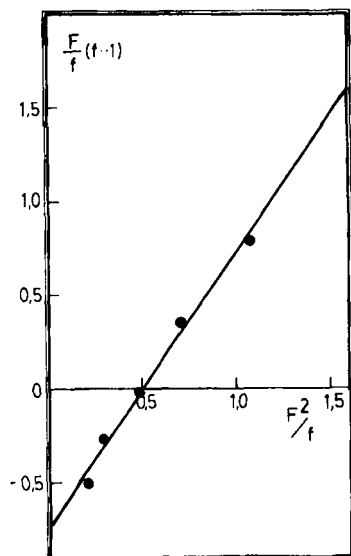
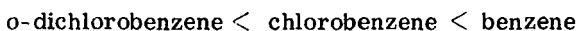


FIG. 2. Fineman-Ross plot of composition results from copolymerization of 1-naphthyl methacrylate and methyl methacrylate in chlorobenzene.

it is to be expected that its coefficients K_{BB} and K_{AA} change in the same way. As it has been pointed out, the methyl methacrylate propagation rate constant K_{BB} is higher in chlorobenzene than in benzene [27] and it is to be expected that the 1-naphthyl methacrylate propagation rate constant K_{AA} increases in a similar way.

As it is shown in Table 2, a good correlation between monomer reactivity ratios and dielectric constant ϵ or dipolar moment μ is evident. An increase of solvent dielectric constant or dipole moment corresponds to an increase of both reactivity ratios which is more pronounced for r_A than for r_B . Bonta [8] and Cameron [5] have suggested that the change of reactivity ratios could be due to the polarity of reaction medium. In the radical copolymerization of methacrylonitrile-styrene, Cameron [5] assumed that the polarity of the propagating methacrylonitrile radicals is sensitive to its environment. In Table 2 the reactivity of monomer A towards B radicals decreases with the solvent polarity in this way:



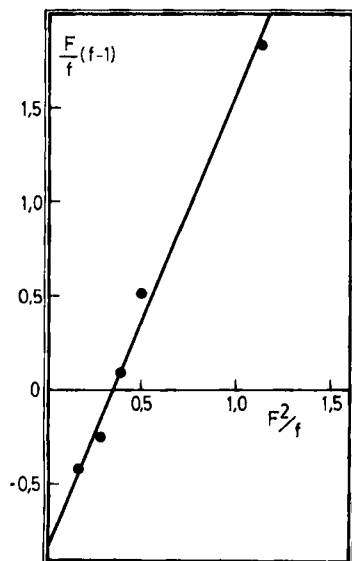


FIG. 3. Fineman-Ross plot of composition results from copolymerization of 1-naphthyl methacrylate and methyl methacrylate in *o*-dichlorobenzene.

TABLE 2. Copolymerization Parameters for 1-Naphthyl Methacrylate (A) and Methyl Methacrylate (B) in Various Solvents at 50°C

Solvent	r_A	r_B	$1/r_A$	$1/r_B$	ϵ	μ
Benzene	1.49	0.66	0.67	1.52	2.275	0
Chlorobenzene	1.50	0.75	0.66	1.33	5.621	1.54
<i>o</i> -Dichlorobenzene	2.45	0.82	0.41	1.22	9.930	2.27

Figure 4 shows $1/r_B$ as a function of solvent dielectric constant and dipole moment; straight lines are obtained, then the increase of r_A could be due to an increase in K_{AA} , and a decrease in K_{AB} as a result of polar solvents will enhance the role of the radical B polarized forms.

The increase of r_B with solvent polarity could be explained in a

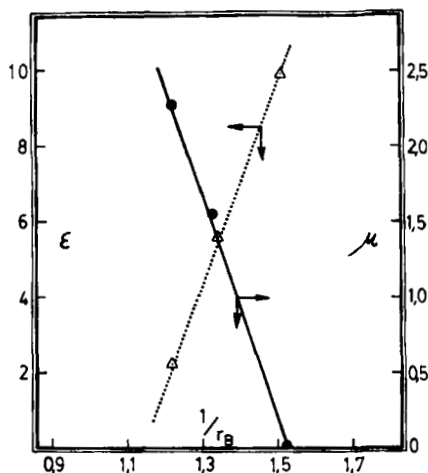


FIG. 4. Effect of the dielectric constant ϵ and dipole moment μ on the relative reactivity of 1-naphthyl methacrylate toward poly-(methyl methacrylate) radicals.

similar way, taking into consideration the competition effects of carbonyl group, with acceptor character and the naphthyl group with donor character.



It is to be expected that the opposite character of the two groups can modify the distribution of electronic charges of naphthyl methacrylate with regard to methyl methacrylate; this means that the polarity of solvent effect will be lower for naphthyl methacrylate than for methyl methacrylate. As is shown in Fig. 5, the polarizability of radical A is only perceptibly affected by a strong change of the solvent dielectric constant.

The copolymer sequences distribution can be determined from

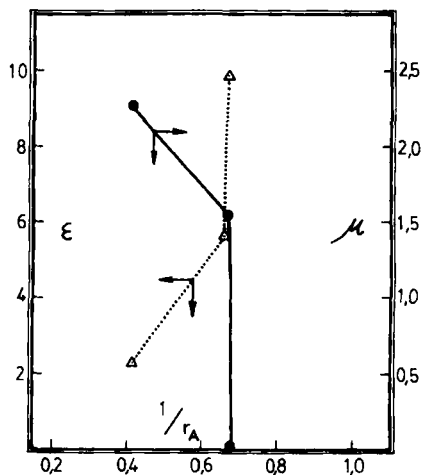


FIG. 5. Effect of the dielectric constant ϵ and dipole moment μ on the relative reactivity of methyl methacrylate toward poly(1-naphthyl methacrylate) radicals.

reactivity ratios of monomers considering the classic theory of statistical probabilities [30]. For copolymers prepared in each of the three solvents used, the following functions have been calculated: number-average sequence length, number-average of alternances per hundred monomer units, run number of Harwood [31], as well as the weight-average functions of sequence distribution of 1-naphthyl methacrylate. The obtained results for several copolymers with the same composition but prepared in different solvents are shown in Table 3, where the great difference between copolymers prepared in *o*-dichlorobenzene in comparison with those prepared in benzene or chlorobenzene can be seen.

The weight-average functions of sequence distribution of 1-naphthyl methacrylate, $W_A(n)$ as a function of the number of units n for copolymers with the same composition prepared in different solvents are reported in Fig. 6. For each one of the composition ratios plotted, $X = 0.43$ and $X = 1.50$, the same curves are obtained for benzene and chlorobenzene, but there are marked differences when *o*-dichlorobenzene is used as solvent. For a composition ratio $X = 0.43$, corresponding to 30 mole % 1-naphthyl methacrylate, the copolymers prepared in benzene or chlorobenzene give a narrower distribution curve than when *o*-dichlorobenzene is used as solvent. The obtained

TABLE 3. Statistical Parameters for 1-Naphthyl Methacrylate (A)-Methyl Methacrylate (B) Copolymers as Calculated from the Reactivity Ratios

Solvent	$X = A/B$	$\bar{\ln}(A)$	$\bar{\ln}(B)$	R
Benzene	0.250	1.37	3.64	39.9
Benzene	0.667	2.00	1.98	50.2
Benzene	1.500	3.24	1.44	42.7
Benzene	2.333	4.48	1.28	34.7
Chlorobenzene	0.250	1.37	4.00	37.2
Chlorobenzene	0.667	2.00	2.12	48.4
Chlorobenzene	1.500	3.25	1.50	42.0
Chlorobenzene	2.333	4.50	1.32	34.3
o-Dichlorobenzene	0.250	1.61	4.27	34.0
o-Dichlorobenzene	0.667	2.63	2.23	41.1
o-Dichlorobenzene	1.500	4.67	1.55	32.1
o-Dichlorobenzene	2.333	6.71	1.35	24.7

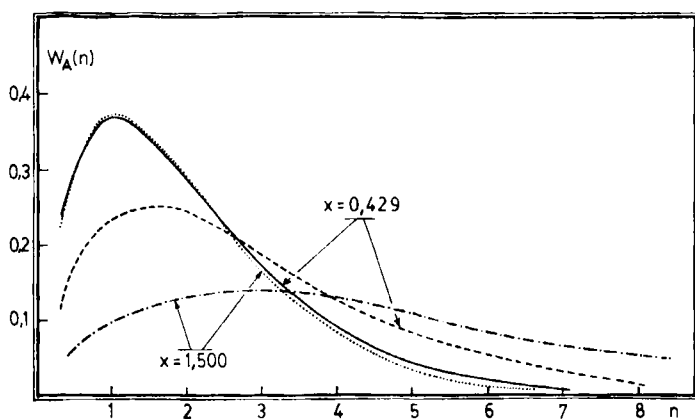


FIG. 6. Weight fraction $W_A(n)$ of 1-naphthyl methacrylate sequences with length n as a function of n : (—) $x = 0.429$, solvent benzene, chlorobenzene; (- -) $x = 0.429$, solvent o-dichlorobenzene; (· - ·) $x = 1.500$, solvent benzene, chlorobenzene; (· · ·) $x = 1.500$, solvent o-dichlorobenzene.

distribution function corresponding to copolymers prepared in benzene and chlorobenzene exhibits a well defined maximum for 1-naphthyl methacrylate sequences only one unit long. However, the copolymers prepared in *o*-dichlorobenzene with the above mentioned ratio $X = 0.43$ (30 mole % of 1-naphthyl methacrylate) give a much wider curve distribution than the copolymers prepared in benzene and chlorobenzene and exhibit a slightly pronounced maximum for $n = 1.5$.

The differences are still more enhanced if we consider the obtained results for such a monomer ratio as $X = 1.50$ (60 mole % of 1-naphthyl methacrylate). Whereas copolymers prepared in benzene and chlorobenzene give a much wider sequence distribution curve than the above mentioned cases, with a poor badly defined maximum to n values between 3 and 4 units of 1-naphthyl methacrylate, it is noteworthy when *o*-dichlorobenzene is used as solvent the sequence distribution curve is close to that obtained for copolymers prepared in benzene and chlorobenzene with a monomer ratio of $X = 0.43$.

The results displayed up to this time allow us to state that the enhancement of polarized forms of the growing radicals, or acceptor monomers by the polarity of solvents and the slight difference of monomer polarity by the nature of functional ester group can explain the microstructural differences of the obtained copolymers.

The glass transition temperature of copolymers often fit equations which are based on the assumption that a fixed amount of free volume is associated with each type of monomer unit. An example is the equation of Fox [32]:

$$\frac{1}{T_g} = \frac{W(A)}{T_g(A)} + \frac{W(B)}{T_g(B)} \quad (1)$$

where T_g is the glass transition temperature of the copolymer and $T_g(A)$ and $T_g(B)$ are those of the corresponding homopolymers. The weight fractions of A and B units in the copolymer are $W(A)$ and $W(B)$. This equation shows a gentle monotonic curve when T_g is plotted against $W(A)$. Fox derived this equation as a simple means to predict polymer glass transition temperatures and with several co-workers contributed to many of the other glass transition prediction equations published in the following years.

These equations include the Gordon-Taylor-Wood [33] type of relationship based also on free volume concepts and it is expressed as in Eq. (2):

$$[T_g - T_g(B)] W(B) + K[T_g - T_g(A)] W(A) = 0 \quad (2)$$

TABLE 4. Transition Temperature of 1-Naphthyl Methacrylate (A)-Methyl Methacrylate (B) Copolymers

Solvent	X = A/B	W (A)	T _g copolymer (°C)
Benzene, chlorobenzene	0.250	0.394	116.5
	0.428	0.568	122.0
	0.666	0.672	122.5
	1.000	0.765	127.0
	1.500	0.817	129.0
	2.333	0.865	130.0
o-Dichlorobenzene	0.250	0.439	117.0
	0.428	0.575	123.0
	0.666	0.713	125.0
	1.000	0.815	127.0
	1.500	0.865	130.0
	2.333	0.912	132.0

where the value K is a constant only for the copolymer under consideration and is related to the specific volume of each homopolymer at its T_g [33].

The Fox relationship and other similar ones assume that the freedom of rotation and free volume contributed to a copolymer by a given monomer will be the same as it contributes to the homopolymer. This is not the case in most polymers, and other theories have been developed based on these considerations. Later Kanig [34] published a modified Fox relationship considering the polymer melt as a mixture of chains and holes and calculated the work required to form a hole by breaking the A-A, A-B, or B-B chains. This approach is limited by the lack of a ready means to obtain A-B bond breaking energies.

As reported by Johnston in 1969 [35], to predict accurately the glass transition temperature of many copolymers it is necessary to take into consideration the sequence distribution of the copolymer. Homopolymer T_g values usually hold for AA dyads in AB copolymers because the A units experience much the same interactions as in A

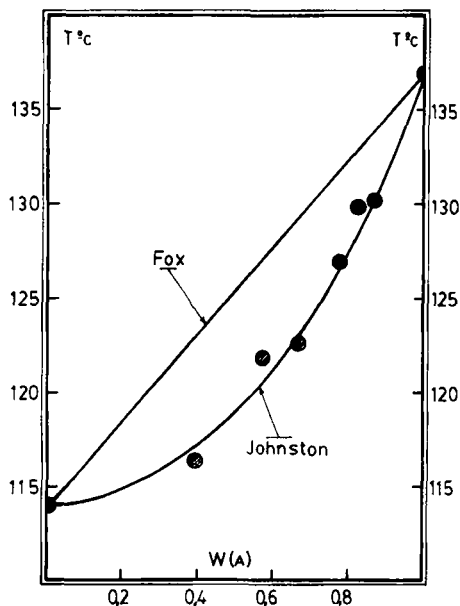


FIG. 7. T_g predicted from Fox equation and sequence distribution equation for 1-naphthyl methacrylate-methyl methacrylate copolymers as a function of the 1-naphthyl methacrylate content in copolymers prepared in benzene and chlorobenzene: (●) experimental points.

homopolymers. The formation of AB dyads results in new interactions and in many cases increases or decreases the T_g contribution of the A unit. Therefore, to obtain more accurate T_g predictions, it is necessary to assign to AB dyads and other sequence distributions their own T_g values.

The equation derived by Barton [36] taking into account the distribution of A and B units in the copolymer could be considered as a logical extension of the Gibbs-DiMarzio theory [37] and is expressed as follows:

$$T_g(P) = N(AA) T_g(AA) + N(BB) T_g(BB) + [N(AB) + N(BA)] T_g(AB) \tag{3}$$

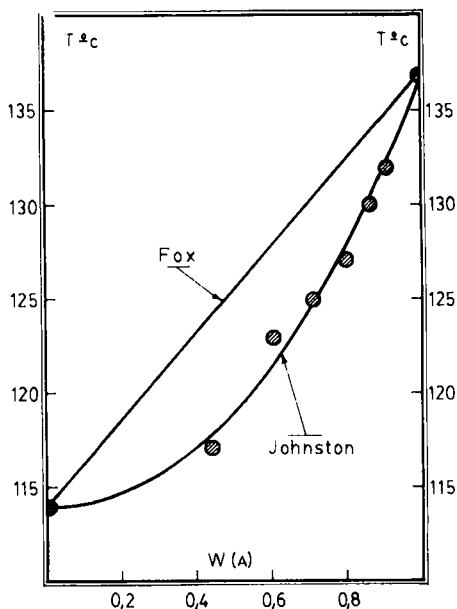


FIG. 8. T_g predicted from Fox equation and sequence distribution equation for 1-naphthyl methacrylate-methyl methacrylate copolymers as a function of the 1-naphthyl methacrylate content in copolymers prepared in *o*-dichlorobenzene: (•) experimental points.

where $T_g(P)$ is the glass transition temperature of the copolymer containing mole fraction N of dyads (AA, BB, AB, BA) respectively; $T_g(AA)$, $T_g(BB)$, and $T_g(AB)$ are considered the T_g of the homopolymers A and B and of the an AB alternating copolymer, respectively.

Finally Johnston [18] has derived a relationship using the probabilities of having various linkages $P(AB)$, $P(AA)$, etc. to predict the copolymer glass transition that could be considered as a generalization of the Fox equation. It is expressed by Eq. (4):

$$\frac{1}{T_g(P)} = \frac{W(A) P(AA)}{T_g(AA)} + \frac{W(B) P(BB)}{T_g(BB)} + \frac{W(A) P(AB) + W(B) P(BA)}{T_g(AB)} \quad (4)$$

where $P(AA)$, $P(BB)$, and $P(AB)$ are the probabilities of formation of

dyads AA, BB, and AB, respectively. For the majority of cases it was found that using a $T_g(AB) = T_g(BA)$ value for AB dyads is enough to predict sequence distribution- T_g effects in a series of copolymers.

In this work, we compare the Fox [32] and Johnston [18] relationships with the experimental results obtained for 1-naphthyl methacrylate-methyl methacrylate copolymers. The glass transition temperatures for the different weight fractions of units A and B in the copolymers are quoted in Table 4.

On the basis of Johnston's interpretation [18] treating the copolymer as a sequence of units AA, BB, and AB, Eq. (4) has been fitted to the experimental data by varying $T_g(AB)$ until the best fit was obtained. All other parameters in the Eq. (4) are known: $P(AA)$, $P(BB)$, and $P(AB)$ have been calculated from well known equations [18].

The best value of $T_g(AB)$ corresponds to a temperature of $387 \pm 1^\circ\text{K}$. The lines calculated with this value are shown in Figs. 7 and 8 where the good agreement between the experimental data and Johnston theory can be seen.

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Accepted by editor December 28, 1978

Received for publication February 20, 1979