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Polymer conformation and viscometric behaviour
6. Synthesis, characterization and chain flexibility of (phenyl methacrylate-co-menthyl methacrylate) copolymers

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SUMMARY

Phenyl methacrylate-co-Menthyl methacrylate copolymers of different compositions were synthetized by radical polymerization in benzene at 298°K. Copolymers from three different compositions were fractionated by solubility. Number average molecular weights $\bar{M}n$ were obtained by osmometric measurements. The Mark-Houwink-Sakurada (MHS) equations were established in benzene at 298°K and the unperturbed dimensions determined by using the Stockmayer-Fixman extrapolation. From these results, the rigidity parameter σ was determined. The results show that the rigidity of the copolymers increase when the menthyl methacrylate content increase, and this is discussed in terms of specific interactions between the different units of the chain. The influence of the nature of the side group and their steric hindrance to rotation is also discussed.

INTRODUCTION

The solution properties of random copolymers show very complex behaviour (1-5). The copolymer composition, the monomer sequence, the nature of the side groups, the specific interactions between the comonomers units, the polydispersity of the fractions, and the molecular weight distribution, are the main factors which influence the behaviour of the copolymers in solution. These factors are very important to consider in the conformational and thermodynamic analysis of these systems. Therefore it is very difficult to estimate the K_Θ and B parameters dealing with the conformation and thermodynamic behaviour of the copolymers.

It has been shown (6-7) that the unperturbed dimensions of random copolymers are affected by the specific interaction between the comonomer units, and they are higher than that of the corresponding homopolymers. In the case of block copolymers, there is a linear relationship between the properties of the corresponding homopolymers (8). Polymethacrylates with aromatic side groups show higher chain rigidity (9-10) than the alicyclic analogues. For instance, poly(menthyl methacrylate) shows higher rigidity than poly(2-tert-butylphenyl methacrylate), which has been explained in terms of specific interactions in the case of aromatic polymers and due to the particular conformation of the alicyclic groups.Furthermore the presence of certain substituents could introduce some changes in the intensity of specific interactions (9).

Aromatic polymethacrylates, containing ortho substituents, show a great steric hindrance to rotation and therefore a significant rigidity factor, which is reflected in different solution properties (11). However

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there is no systematic study about the effect of this kind of factors on the conformational and thermodynamic behaviour of methacrylic copolymers containing aromatic and alicyclic side chain (12).

In this work we report the solution properties and the conformational behaviour of phenyl methacrylate-co-menthyl methacrylate copolymers in order to investigate the effect of the copolymer composition on the conformational properties in comparison with those of the corresponding homopolymers studied previously.

EXPERIMENTAL

Menthyl methacrylate (MeM) was synthetized from methacryloyl chloride and menthol according to the method described by Burtle and Turek (13). Phenyl methacrylate (PhM) was prepared by the reaction of phenol and methacryloyl chloride according to the technique described by Patai (14). All the solvents used were analytical grade and previously purified. The copolymerizations were carried out by using AIBN as the initiator at 50°C in a pyrex tube into which the mixture of monomers dissolved in benzene was sealed under vacuum. The reaction was stopped at small conversion degree. All copolymers dissolved in benzene were purified by reprecipitation with methanol.

The molar ratio of monomers in feed, the composition, the conversion, and the intrinsic viscosities $[\eta]$ are listed in Table 1. The composition of the copolymers was determined by infrared analysis with a Perkin-Elmer 567 IR Spectrophotometer.

The copolymers CP-1, CP-2 and CP-6 were fractionated by fractional precipitation by using benzene/methanol as solvent mixture. The composition of each fraction was checked by IR analysis, and no variation due to the fractionation was detected.

A Hewlett-Packard High Speed membrane osmometer model 502 was used to determine the number average molecular weight of the copolymer at 298°K in toluene. In order to control the polymolecularity of some fractions, weight average molecular weights, $\bar{M}w$, were obtained by size-exclusion chromatography.

Intrinsic viscosity measurements were performed by using a Desreux-Bischoff (15) capillar dilution viscometer. Neither kinetic energy or non-Newtonian corrections were found to be necessary. The intrinsic viscosity $[\eta]$ was determined by extrapolation according to the classical Huggins and Kraemer equations.

The microtacticity of the homopolymers are similar to that of the samples used by Tricot (9) and Niezette (16). The percentages of triads mm, mr and rr are 15%, 40% and 46% respectively.

RESULTS AND DISCUSSION

Number average molecular weight $\bar{M}n$, the reduced osmotic pressure at infinite dilution, and intrinsic viscosity $[\eta]$ in dlg^{-1} for the fractions of the three copolymers are summarized in Table 2. The number average molecular weights $\bar{M}n$ have been calculated according to the classical relation for osmotic pressure measurements (17-18) from π/c versus c plots. Figure 1 shows the log-log plots of intrinsic viscosity versus molecular weight according to the Mark-Houwink-Sakurada (MHS) equation. With the low polymolecularity of the fractions ($\bar{M}n/\bar{M}n<1.3$) there are not essentially changes in MKS relationship and other properties vs molecular weight rel-

TABLE 1. Polymerization data for PhM-MeM copolymers

Copolymer Sample	Molar ratio in feed x= (PhM)/(MeM)	Conversion (%)	MeM in products mole fraction	MeM (%)	$[\eta]^a$
CP-1	1.39	5.35	0.40	48	0.85
CP-2	3.08	6.14	0.17	22	1.08
CP-3	0.99	6.22	0.45	53	0.53
CP-4	0.72	5.43	0.57	65	0.47
CP-5	0.81	8.30	0.51	62	0.99
CP-6	0.40	7.70	0.74	80	0.83

a: $dl \cdot g^{-1}$, in benzene at 298°K.

TABLE 2. Reduced osmotic pressure at c=0, Number Average Molecular Weight $\bar{M}n$ and intrinsic viscosity $[\eta]$ for fractions of copolymers CP-1, CP-2, and CP-6.

Copolymer	Fraction	$(\frac{\pi}{c})_{c=0}^{a}$	$\bar{M}n \cdot 10^{-5}$	$[\eta]^b$
CP-6	CP-80-1	0.19	15.32	1.66
	CP-80-2	0.30	9.70	1.14
	CP-80-3	0.47	6.19	0.85
	CP-80-4	0.98	2.97	0.57
CP-1	CP-48-1	0.29	10.04	1.39
	CP-48-2	0.42	6.93	0.94
	CP-48-3	0.73	3.99	0.69
	CP-48-4	2.02	1.44	0.38
CP-2	CP-22-2	0.33	8.82	1.19
	CP-22-3	0.46	6.33	0.93
	CP-22-4	0.66	4.41	0.69
	CP-22-5	0.94	3.10	0.57

a: in toluene at 298°K; b: dlg^{-1} in benzene at 298°K ationships. The values of the K_a and a parameters in benzene at 298°K are shown in Table 3. Experimental points of the MHS equation show straight lines and the values of the Ka and a parameter are in the ordinary range for linear flexible polymers. The viscosimetric behaviour of these copolymers is similar to that of the corresponding homopolymers (19-20).

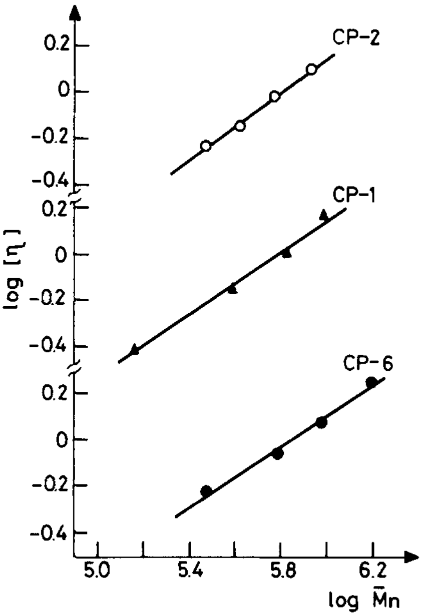

Fig.1. Mark-Houwink-Sakurada relationships for the copolymers in benzene at 25°C.

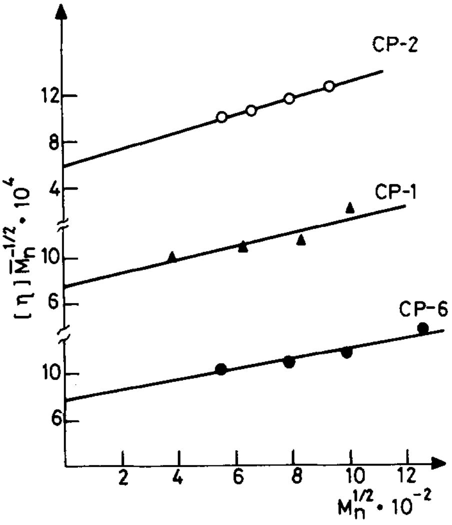

Fig.2. Stockmayer-Fixman plots for the copolymers in benzene at 25°C.

It is interesting to note that the a values, hence the solvent power of benzene to the copolymers, decreases as the menthyl methacrylate composition increases. These results show that the copolymer chain are less extended in a given solvent than the corresponding homopolymer chains. It is difficult to explain this behaviour although the a values for the homopolymers are quite similar. We cannot discard the possibility of an interaction among the like units of the copolymer. Similar results have been found in other vinylic copolymers (1). These results suggest that the conformational behaviour of the copolymers could be of interest in order to clarify the thermodynamic behaviour of their solutions.

In order to find the value of the conformational parameter K_Θ, leading to the unperturbed dimensions $\langle r^2\rangle_o^{1/2}$, given by

$$K_\Theta = \Phi_o (\langle r^2\rangle_o/M^{3/2}) = [\eta]_\Theta/M^{1/2} \qquad (1)$$

the Stockmayer-Fixman (21) equation was employed.

TABLE 3. K_a and a parameters from the MHS relation for homopolymers and copolymers in benzene at 298°K.

Polymer	$K_a \cdot 10^5$	a
PMeM (19)	9.6	0.67
CP-6	16.9	0.64
CP-1	17.3	0.65
CP-2	7.3	0.71
PPhM (20)	5.7	0.72

TABLE 4. Unperturbed dimensions, rigidity parameter σ, and thermodynamic parameter B for homopolymers and copolymers in benzene at 298°K.

Polymer	$K_\Theta \cdot 10^4$ a		$(\langle r_0^2 \rangle / M)^{1/2} \cdot 10^{11}$		σ		$B \times 10^{28}$
	Exp.	Ideal	Exp.	Ideal	Exp.	Ideal	
PMeM (19)	4.4		614		3.10		0.56
CP-6	7.7	4.64	740	624	3.49	3.00	2.87
CP-1	7.6	5.02	737	641	3.29	2.89	3.83
CP-2	5.9	5.34	677	654	2.89	2.81	4.92
PPhM (20)	5.6		665		2.75		6.35

a: $dl^{3/2}\ g^{-2/2}\ mol^2$

The plots are given in figure 2. The values of K_Θ obtained by this relation for the three copolymers studied and the corresponding homopolymers are listed in Table 4, which also shows the unperturbed root mean-square end-to-end dimensions.

If the unperturbed average dimensions of a copolymer chain conformed to an idealyzed random flight model consists of two different kind of independent statistical chain elements, the unperturbed mean-square end-to-end distance and, therefore the parameter K_Θ would obey to a relation (2,22) of the type:

$$[K_\Theta]_{co} = X_A K_{\Theta A} + X_B K_{\Theta B} \qquad (2)$$

where X_A and X_B are the weight fractions and $K_{\Theta A}$ and $K_{\Theta B}$, are the conformational parameter K_Θ characteristic of the homopolymers.

The $[K_\Theta]_{co}$ values estimated for CP-6, CP-1 and CP-2 from the above expression are also summarized in Table 4, where they are labeled K_Θ ideal. Table 4 shows that the K_Θ values obtained from the Stockmayer-Fixman equation are much larger than those expected from equation 2. The characteristic ratio $(\langle r^2\rangle_o^{1/2}/M)^{1/2}$ of the copolymers increase as the MeM content increase. Apparently, the introduction of menthyl units into PPhM bring about a very large increase of the average dimensions. The same behaviour has been reported by Utiyama (23) for styrene-methyl methacrylate random copolymers and by Radic et al (1) for tert-butylphenyl methacrylate-vinyl-pyrrolidone copolymers. These results demonstrate once again that the unperturbed dimensions of copolymers are a function of the copolymer composition, the sequence length distribution, and the stereochemical configuration as Kotaka et al (6) pointed out.

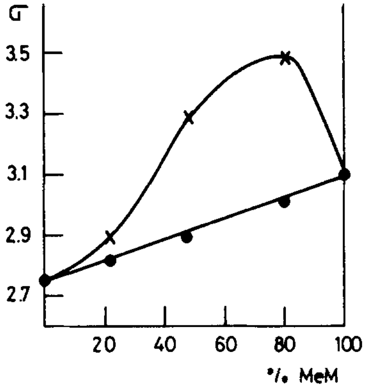

Fig.3. Variation of the rigidity parameter of the copolymers as function of the MeM content. (●) calculated values; (x) experimental values.

The values of $\langle r^2\rangle_o^{1/2}/\langle r^2\rangle_{of}^{1/2}=\sigma$ that represent the effect of the steric hindrance on the flexibility of the chain are also shown in Table 4, where the ideal value is that calculated from the values of ideal unperturbed dimensions. The experimental σ values are higher than calculated, as it can be seem in figure 3, in which we can see that the copolymer containing 80% of MeM (CP-6) shows the higher rigidity. These results confirm that the steric hindrance increase as menthyl groups are incorporated to the polymer chain.

The long range interaction parameter was also estimated from the Stockmayer-Fixman plots and the results are summarized in Table 4. This parameter, which reflect the polymer-solvent interaction, shows the same trend that a parameter of the MHS equation, i.e., B diminished as the content of MeM increases. This result would indicate that the number of segment-solvent contacts decrease as the menthyl groups increase, due to the different solvent quality of benzene for the copolymers.

For a binary copolymer the excluded volume parameter in the Stockmayer-Fixman equation may be written as a quadratic function of composition:

$$B= X_A^2 B_A + (1-X_A)^2 B_B + 2X_A (1-X_A) B_{AB} \qquad (3)$$

where B_{AB} characterizes long-range interaction between unlike monomers (2-6).

To a first approximation, we estimate the excess interaction term ΔB_{AB}, according to:

$$\Delta B_{AB}= B_{AB}-(B_A-B_B)/2 \qquad (4)$$

where B_{AB} is calculated from equation (3) for the different copolymers. The term ΔB_{AB} is supposed to be dependent of the solvent only through its molar volume, and is characteristic of the monomer species (6). Taking an average value for B_{AB}, as other workers (2-6) have done in making comparisons, we have an approximate value of $1{,}2\cdot 10^{-28}$ for ΔB_{AB} in benzene. The positive ΔB_{AB} implies the existence of repulsive interactions between the comonomers (2). However for the copolymer with low menthyl composition ΔB_{AB} is negative, which means that at this composition there are attractive interactions. This could be explàned by taking into account that the menthyl units are very dilute in the polymer chain and therefore the interactions of phenyl would predominate.

Finally we can conclude that these polymers behave as linear flexible polymers from a viscometric point of view. The introduction on menthyl units in the chain diminishes the a exponent of the MHS equation and therefore, the solvent power diminishes. The conformational analysis of these copolymers show an increase of the unperturbed dimensions when the menthyl units increase. It is necessary to take into account that the introduction of menthyl groups apparently introduce some degree on flexibility, but as the menthyl groups are very bulky and their molar volume is higher than that of phenyl groups, there is an increment of the rigidity.

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