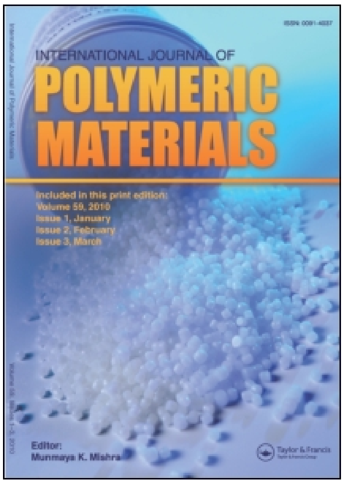

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FT-RAMAN CHARACTERIZATION OF METHYL ACRYLATE-ETHYL ACRYLATE COPOLYMERS

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FT-RAMAN CHARACTERIZATION OF METHYL ACRYLATE-ETHYL ACRYLATE COPOLYMERS

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Vibrational spectra of a series of Methyl Acrylate/Ethyl Acrylate (MA/EA) copolymers, synthesized at 60°C and 70°C for 5 different MA/EA compositions for each temperature, were obtained by FT-Raman spectroscopy. An inversion of the symmetric and antisymmetric stretching vibrations of the CH_3 group, due to the mobility of this group, was found. By analyzing the acoustical and optical branches of the spectra, the mobility of the backbone structure was also determined. The EA homopolymer was found to posses the highest conformational order.

Keywords: FT-Raman, vibrational spectra, Methyl Acrylate-Ethyl Acrylate copolymers, conformation, mobility

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INTRODUCTION

Acrylic materials have been employed in a wide range of applications from coatings to adhesives and paints, due, among other reasons, to their endurance and outdoors durability, along with the important fact that practically no solvents are liberated by these materials. Nevertheless, during the past decade or so, a renewed interest in novel applications of acrylic systems has arisen, among which one can mention composite materials based on an acrylic matrix and a broad range of particles, including metals, graphite, carbon black, fibers, bioceramics, etc., aimed to produce engineering materials with improved properties [1,2], for applications such as optical devices [3] and even biomaterials [4]. In all those cases, however, a key parameter for achieving a working composite is related to the details of the synthesis of acrylic systems involved [5,6], for many interfacial properties between the matrix and the particles have to do with the conformational structure of the matrix itself. Accordingly, the present work is aims to study the structural characteristics of Methyl Acrylate/Ethyl Acrylate (MA/EA) copolymers as a function of the different compositions and synthesis conditions, through the vibrational spectra as obtained by FT-Raman spectroscopy.

EXPERIMENTAL

A. Materials

EA and MA monomers were obtained from Celanese® de México S.A. Sodium Diclorohexilsulfonate was employed as surfactant, Potassium Persulfate as initiator, buffers solution was Sodium Bicarbonate and Hydroquinone was utilized as inhibitor. All these chemicals were supplied by Quimir.®

B. Polymerization Route

Copolymers were synthesized according to a previously reported method [5,6] with the MA/EA weight compositions 100/0, 75/25, 50/50, 25/75 and 0/100, for both 60 and 70°C.

C. FT-RAMAN Spectroscopy

Films were cast with each one of the above systems at room temperature. The films were rolled over to form cylinders 2.5 cm long and 0.5 cm in diameter, and were analyzed in a Nicolet 910 equipped with a 200 mW laser operating at 1064 nm, a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the spectra corresponding to the concentrations: (a) 100/0, (b) 50/50 and (c) 0/100, weight percentage MA/EA synthesized at 60°C, along with the chemical structure of the corresponding

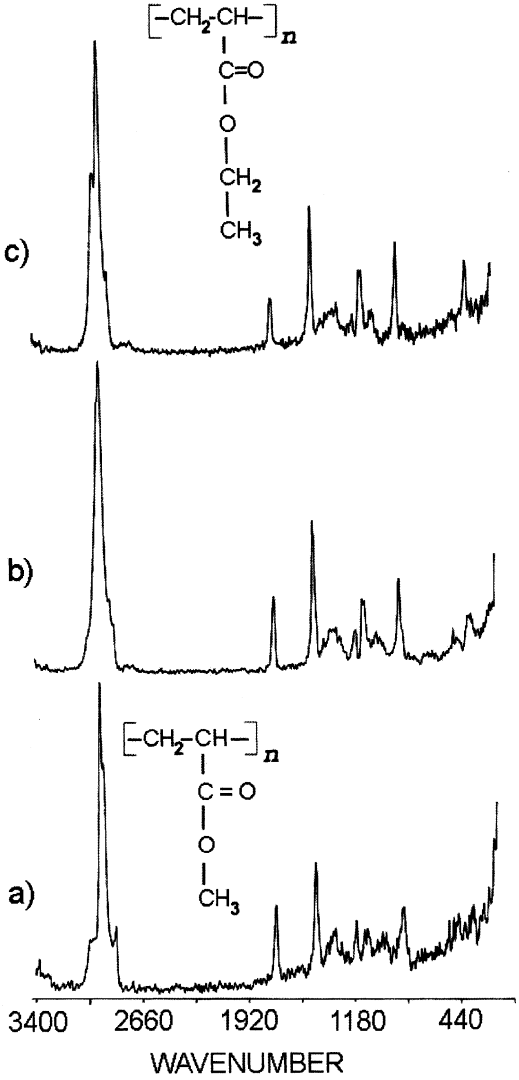

FIGURE 1 FT-Raman spectra of MA/EA copolymers synthesized at 60°C. Weight percentage compositions of: (a) 100/0, (b) 50/50 and (c) 0/100.

homopolymers. Due to Fermi resonance [7] and to the superposition of the various vibrational modes, the spectra of each one of the homopolymers are rather complex. However, as will be shown below, it is possible to deduce the situation in the copolymers. In fact, Figure 2

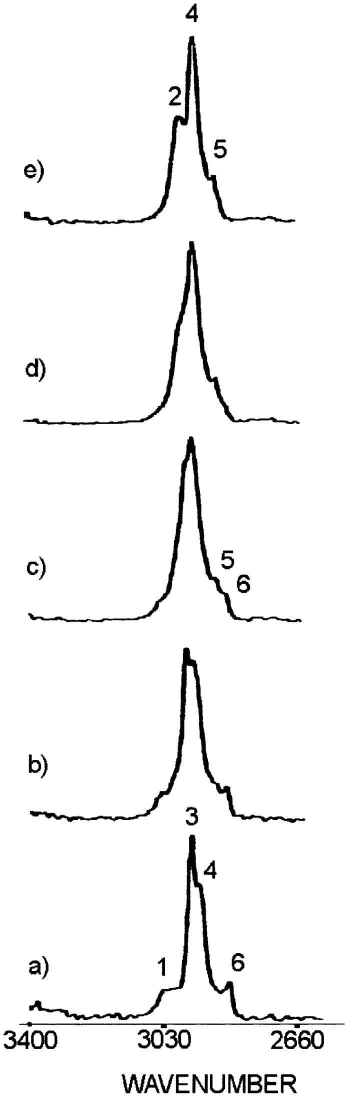

FIGURE 2 Stretching region of the FT-Raman of MA/EA copolymers synthesized at 60°C. (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75 and (e) 0/100.

contains the bands corresponding to high wave numbers (i.e. stretching region ν, of the CH) for the series synthesized at 60°C. Band 1 corresponds to a shoulder originated by the vibration of the O-CH_3 group, which vanishes as the concentrations of that group decrease. The most intense band (#3) corresponds to the composition MA/EA:100/0 and it is assigned to an in-plane asymmetrical stretching of the methyl group [9], ν_a CH_3. This vibration presents a shift towards a more energetic region, band 2, in the other homopolymer (MA/EA:0/100), corresponding now to an out-of-plane ν_a CH_3 vibration, since the group is longer and with higher mobility. The methyl symmetric vibration, ν_a CH_3, is found in band 4, has the second highest intensity for the 100/0 concentration and increases as band 3 decreases, producing a sort of swinging behavior.

Band 5 appears as a weak shoulder in the MA homopolymer and corresponds to an asymmetric vibration of the methylene group, ν_a CH_2. In contrast, a well−defined peak for the symmetric stretching of methylene group, ν_a CH_2 is observed in band 6. As the concentration of AE increases, the shoulder becomes stronger.

Figure 3 shows the spectra of the low and medium wavenumbers region (i.e. below 700 cm^{-1} and within the range 1750−700 cm^{-1}, respectively) for copolymers synthesized at 60°C. Peaks 7 and 8 correspond to the carbonyl stretching modes, ν C=O, and methylene bending, δ CH_2, the Lattex superimposed on δ CH_3. The broad band 9, assigned to the superposition of methylene wagging, ω CH_2 and methyl bending, δ CH_3 show a rather complicated behavior. The weak peak 10 methylene twisting, τ CH_2, is slightly shifted due to the structural changes induced by the variation of density of methylene groups in the copolymers. The superposition of methylene and methyl rocking modes, ρ $CH_2 + \rho$ CH_3 in band 11, decreases in intensity and shifts its positions due to the same effect.

Bands 12, 13 and 14, and even the small shoulder in 1072 cm^{-1}, represent the optical vibrations of the backbone. Bands 12 and 14 correspond to a trans-confirmation, whereas band 13 to a gauche [11−14]. The relation of intensities 13 to 14 or 12 to 14 increases as the concentration of ethyl groups increases, reflecting an increase in the conformational order [12], that is, the density of trans conformers, increases [14]. This is an interesting finding since it indicates that, in spite of being perfect solids, these copolymers exhibit a liquid-like behavior, which can be controlled by the MA/EA relationship.

Two doblets can be appreciated, one in band 15, corresponding to a CH_2 wagging vibration, superimposed to a non-identified vibration, whereas in band 16 the C-O-C and C-C-C stretching modes are superimposed. The doblet of band 15 disappears as the content of ethyl

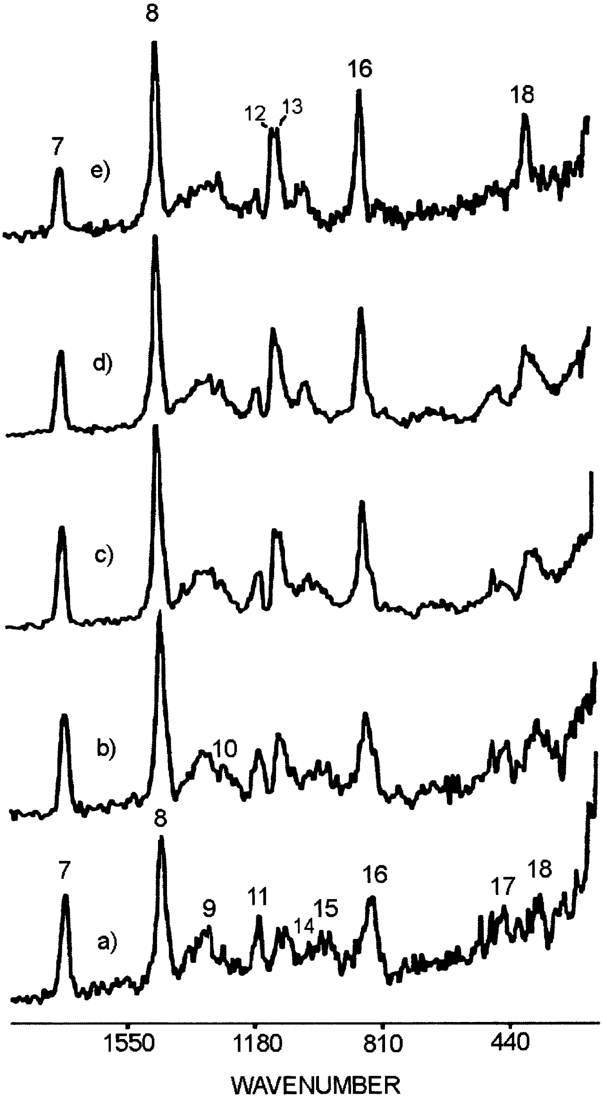

FIGURE 3 FT-Raman spectra of MA/EA copolymers (a) 100/0, (b) 75/25, (c) 59/59, (d) 25/75 and (e) 0/100. Synthesis temperature: 60°C.

groups increases. The doblet in 16 becomes a single peak, due to the effect of the backbone. Two bands appear in the low-wavenumbers region, namely 17 and 18, and the latter corresponds to expansions of the backbone in the acoustic mode. Changes in bands 16 and 18 reinforce the idea that the homopolymer of EA possesses a more ordered structure, as compared to that of the polymethyl acrylate.

Figures 4 and 5 show the spectra for high and medium wavenumbers regions of samples synthesized at 60 and 70°C, respectively.

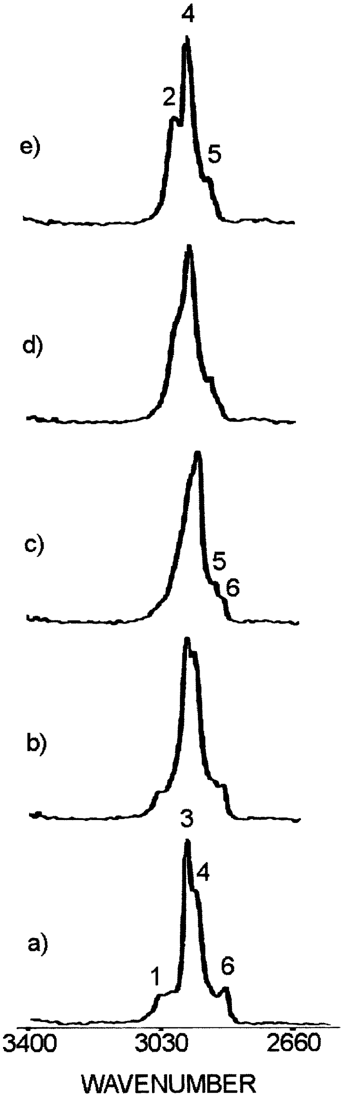

FIGURE 4 Stretching region of the FT-Raman of MA/EA copolymers synthesized at 70°C. (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75 and (e) 0/100.

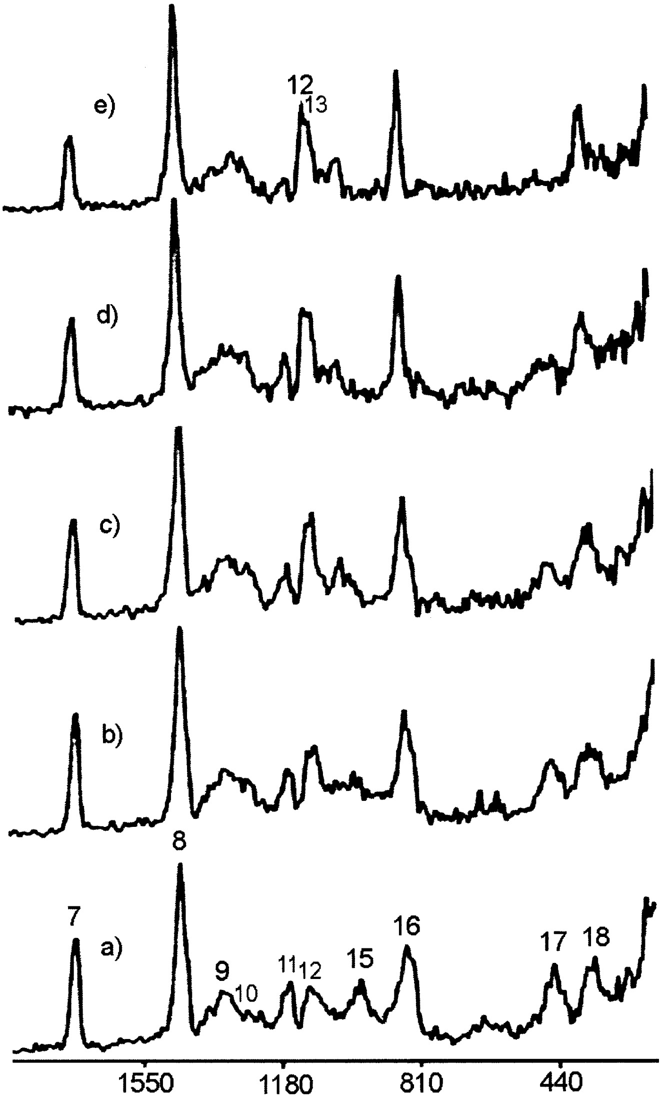

FIGURE 5 FT-Raman spectra of MA/EA copolymers (a) 100/0, (b) 75/25, (c) 59/59, (d) 25/75 and (e) 0/100. Synthesis temperature: 70°C.

As observed there, the behavior is completely similar to that of samples prepared at 60°C. Optical bands (12 to 14) and acoustic band (18) of the backbone structure, indicate also a conformational ordering, depending on the specific composition, similar to the effect of temperature on the homopolymer of MA [15].

TABLE 1 Summary of Raman Bands

	60°C					70°C					
	100/0	75/25	50/50	25/75	0/100	100/0	75/25	50/50	25/75	0/100	Assignment
1	3030	3030	3037	–	–	3030	3030	3030	–	–	ν O-CH$_3$
2	–	–	–	2970	2970	–	–	–	2970	2963	ν_a CH$_3$ out-of-plane
3	2948	2941	2948	–	–	2948	2948	2948	–	–	ν_a CH$_3$ in-plane
4	2926	2926	2926	2926	2926	2933	2926	2926	2933	2926	ν_s CH$_3$?
5	2863	2867	2874	2867	2867	2867	2867	2867	2874	2867	ν_a CH$_2$?
6	2848	2837	2845	2841	–	2852	2845	2837	2852	–	ν_s CH$_2$
7	1732	1732	1732	1732	1732	1732	1725	1732	1725	1725	ν C $=$ O
8	1457	1457	1457	1457	1457	1457	1457	1457	1448	1457	δ CH$_2$ $+$ δ CH$_3$
9	1319	1341	1348	1304	1304	1348	1341	1319	1332	1304	ω CH$_2$ $+$ δ_s CH$_3$
10	1275	1283	1275	1268	1283	1283	1275	1268	1266	1283	τ CH$_2$
11	1166	1174	1159	1159	1167	1167	1167	1159	1166	1159	ρ CH$_3$ $+$ ρ CH$_2$
12	1108	1116	1116	1108	1108	1116	1116	1109	1115	1108	ν C-C(trans)
13	1086	1094	1101	1094	1094	1094	1094	1094	1094	1093	ν C-C (gauche)
14	1013	1000	1022	1014	1022	–	–	1022	1021	1013	ν_a C-C (trans?)
15	993	971	1000	–	–	978	993	993	985	–	ω CH$_2$?
16	833	862	862	855	855	846	862	848	862	862	ν C-O-C $+$ ν C-C-C
17	455	442	478	456	–	456	463	456	–	–	δ C=O(δ COC?)
18	354	355	355	376	376	347	362	355	369	369	Chain expansion

Finally, Table 1 contains a summary of all the band-found and their corresponding assignation. Since the relation of intensities I (ν_a CH_2)/(ν_b CH_2) reveals the degree of mobility of the backbone [11, 16], the results indicate that, surprisingly, the MA homopolymer is more disordered than that of EA.

CONCLUSION

The vibrational behavior of MA/EA copolymers has been studied, revealing that, in the region of high wavenumbers, there is a switch in intensities of the peaks ν_s CH_3 and ν_a CH_3, as a result of the change in mobility of the pendant group due to the increase in EA content. The homopolymer of MA is more disordered than any composition of the copolymer, as well as the EA homopolymer. From the region of medium wavenumbers, one can conclude that the optical and acoustic modes of the backbone indicate a conformational ordering [17] that becomes higher as the concentration of EA in the copolymer increases.

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