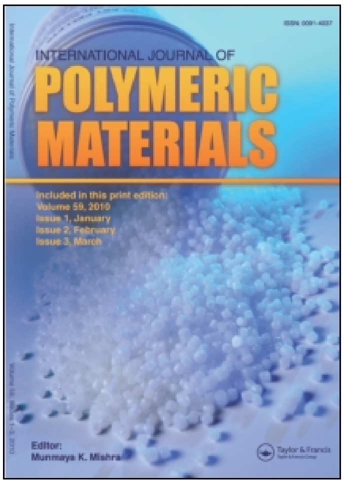

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Synthesis of Ethyl Acrylate-Methyl Acrylate Copolymers via Emulsion Polymerization

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A series of methyl acrylate-ethyl acrylate copolymers were prepared via emulsion polymerization using a batch reactor. Some reaction parameters, such as composition and temperature, were varied in order to determine their influence on the polymerization rate. A high exothermic behavior (Trommsdorf effect) was observed when the temperature was increased. Very stable lattices were obtained and characterized by gravimetry, infrared spectroscopy, quasi-elastic light scattering (QELS), differential scanning calorimetry, and transmission electron microscopy methods. In all cases, monodispersed, small sized particles were obtained. The position annihilation parameters τ_3 *and* I_3 *of all the copolymers were also measured and related with their glass transition temperatures.*

Keywords: Methyl acrylate; ethyl acrylate; emulsion copolymerization; particle size; positron annihilation

INTRODUCTION

Acrylic polymers have many applications in various domains such as coating, adhesives, varnishes, waxes, and paint bases. However, the durability of these materials depends greatly on their resistance to UV radiation degradation.

The synthesis of acrylic polymers can sometimes become suddenly highly exothermic. This phenomenon is known as "Trommsdorff

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effect", which is due to an entanglement of the macromolecular chains during the reaction (1). It inhibits the approach of free radicals toward the end of the polymer chains, and will avoid the reaction termination. Consequently, the free radical concentration increases, and the reaction starts to accelerate exothermically. Very often, during the acrylic synthesis, the high heat exchange is controlled using emulsion polymerization techniques (2), because water, used as a media of dispersion, can absorb the released energy (3). In addition, materials, that are prepared via this technique may be used directly without further purification.

In this paper, the synthesis by emulsion polymerization techniques, performed in a batch reactor, of a series of methyl and ethyl acrylates copolymers (4) are presented together with their characterization. The dependence of the conversion rate, during the copolymerization, on the temperature and monomer feed ratio was also determined.

MATERIALS AND METHODS

Methyl and ethyl acrylates (from Celanese) were used as monomers to synthesize the copolymers. Tertbutylcatechol, an inhibitor contained in the monomers (45 ppm), was eliminated using an excess of $K_2S_2O_8$ (from Aldrich). The monomers were dispersed in the aqueous phase using dodecylbenzensulphonate (from Aldrich) as surfactant. Sodium bicarbonate was employed as tampon, and distilled water as a media of dispersion.

All the polymerizations were performed in a 1 L stirred glass reactor, under a dynamic flow of N_2, and at constant temperatures controlled via a thermal bath. The stirring rate was adjusted to 250 rpm.

The formulation used to prepare all the lattices is shown in Table 1.

The evolution of the monomers conversion was followed by simple gravimetric techniques. The final size of the particles in the prepared lattices was determined using a Z-plus Brookhaven Instrument.

TABLE 1 General Formulation for MeA-EA Lattices with a Solid Content of 20% wt

Components	Substances	Amount (g)
Monomers	MeA-EA	120
Initiator	Solution of Potassium Persulphate (1.2% wt.)	50
Surfactant	Solution of RAFA (2.4% wt.)	150
Buffer	Solution of Sodium Bicarbonate (1.2% wt.)	50
Dispersion medium	Distilled water	230

Samples of the latex were stained with Osmium tetroxide (from Sigma) following a process given elsewhere (5,6). Then, a drop of every sample was deposed on a metallic gria in order to image them by electron transmission microscopy (ETM) using a Jeol JEM-100CX instrument.

Once the copolymers were obtained, the materials were precipitated from the latex using methanol and washed with distilled water. IR spectra of the copolymers were then obtained on a Nicolet 510 FT-IR spectrophotometer. The glass transition temperature of the different copolymers was also measured using a Perkin-Elmer Calorimeter DSC-7.

In order to know the dependence of the free volume on the copolymer composition, a Positron Annihilation Spectrum was obtained by irradiating samples, which were purified, degassed and sealed in a glass tube, with a positron source ($Na^{22}Cl$, 9 Ci radiometric activity). A fast gamma-gamma coincidences system allowed registering the positronium annihilation parameters I_3 and τ_3. The o-Ps formation probability I_3 is proportional to the number of cavities that constitute the free volume of the material, whereas the mean lifetime τ_3 constitutes a measure of the cavities diameters (7). These parameters were calculated on PATFIT88, a program that is commercially available.

RESULTS AND DISCUSSION

Copolymers with monomer ratios of MeA/EA of 100/0, 75/25, 50/50, 25/75 and 0/100% wt. were first synthesized in the batch reactor at 60°C. The evolution of the conversion as a function of the reaction time is summarized in Figure 1, where it can be observed that the polymerization was very fast, especially for the systems having a rich EA feed ratio. Moreover, a polymerization of EA showing a 100% conversion was reached in only 60 minutes. It has to be emphasized that the Tromsdorff effect was not observed during the reactions.

The effect of the temperature on the reaction evolution was also studied by carrying out a series of polymerizations at three different temperatures. The results of the conversion as a function of time obtained for these experiments are presented in Figures 2, 3 and 4, where, as it can be seen, the reaction rate increased with temperature. However, when the polymerization was performed at temperatures higher than 60°C, a strong auto-acceleration was observed and the thermal conditions in the reactor were difficult to control. On the other hand, at temperatures lower than 60°C, the reaction was slower, and complete conversions were only reached after more than 100 minutes.

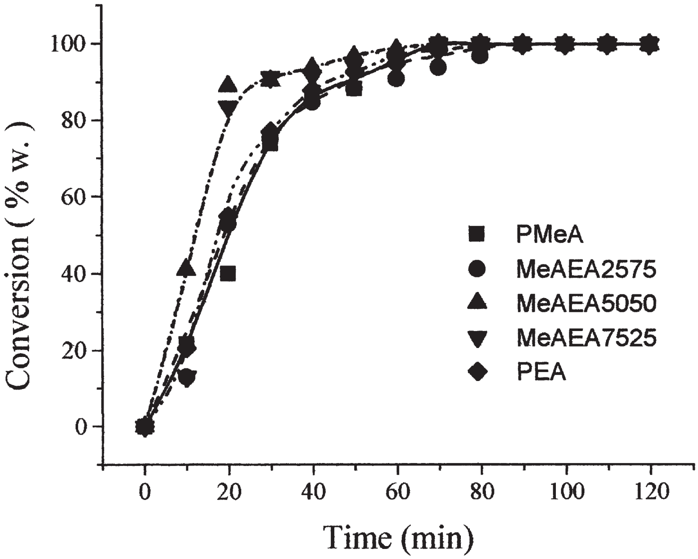


FIGURE 1 Reaction evolution of MeA-EA copolymers obtained at 60°C (MeA/EA: 100/0, 75/25, 50/50, 25/75 and 0/100 w/w.).

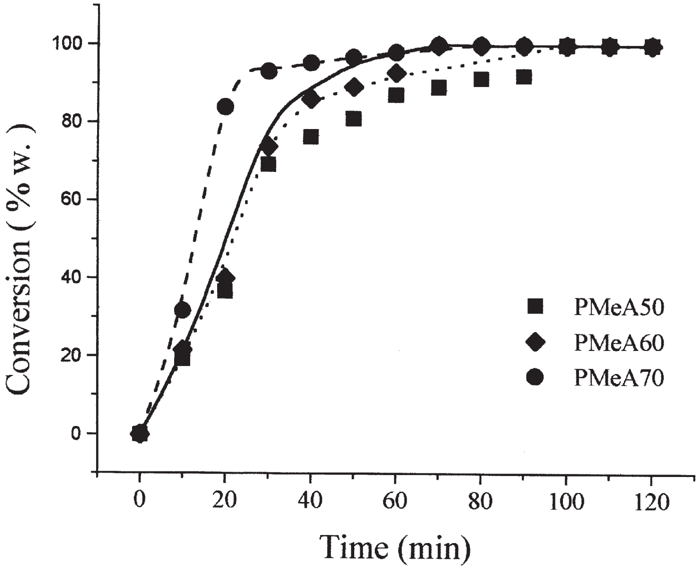


FIGURE 2 Effect of the temperature on the MeA emulsion homopolymerisation (T = 50, 60 and 70°C).

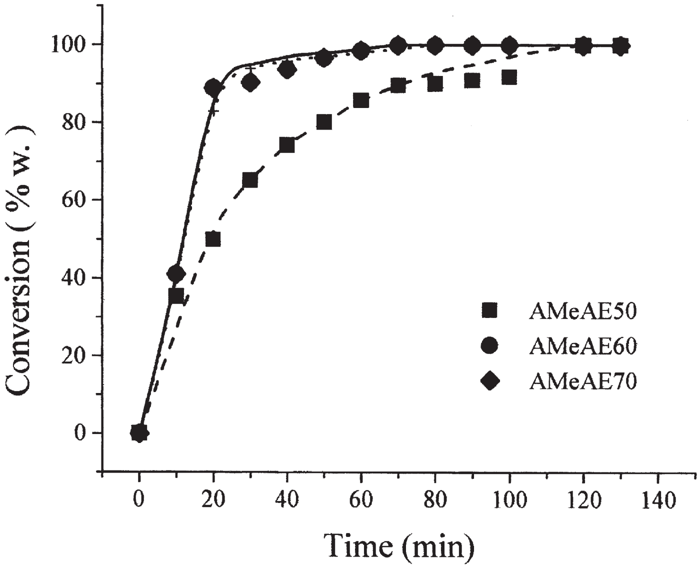


FIGURE 3 Effect of the temperature for the copolymers 50/50 w/w.

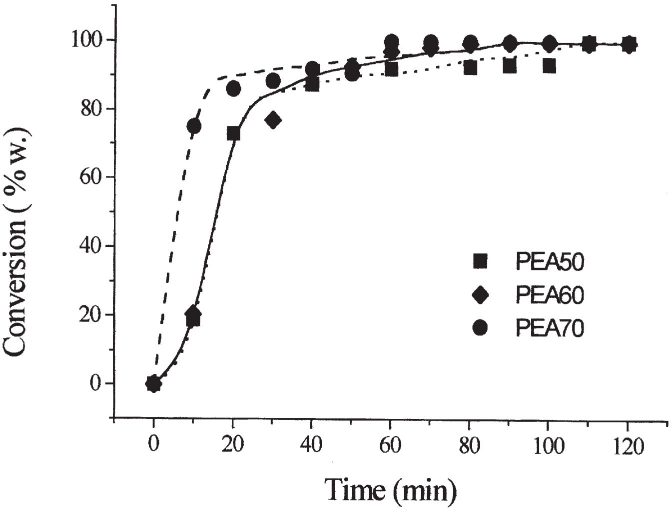


FIGURE 4 Effect of the temperature on the evolution reaction for the EA polymers.

Very stable lattices were obtained from the reactions that reached completion. The particle sizes of every system were determined by QELS, and the number of particles by units of volume was calculated using the following equation:

$$N_p = \frac{6m_0}{\pi \rho_{pol} D_{pz}} \tag{1}$$

Where: m_0: solids content (g/cm^3),
ρ_{pol}: polymer density (g/cm^3),
D_{pz}: average particle diameter (cm)

The number of particles together with their diameters for the copolymer dispersions are reported in Figure 5.

Some ETM micrographs of the latex particles were obtained but are not reproduced here. The imaging of the particles confirmed their size, which was previously determined by QELS, and allowed to observe the monodispersity of the latex particles (8).

From the IR spectra of PEA, poly(ethylacrylate-co-methylacrylate): 50/50 w/w., and PMeA (Figures 6a), b) and c)), two main peaks

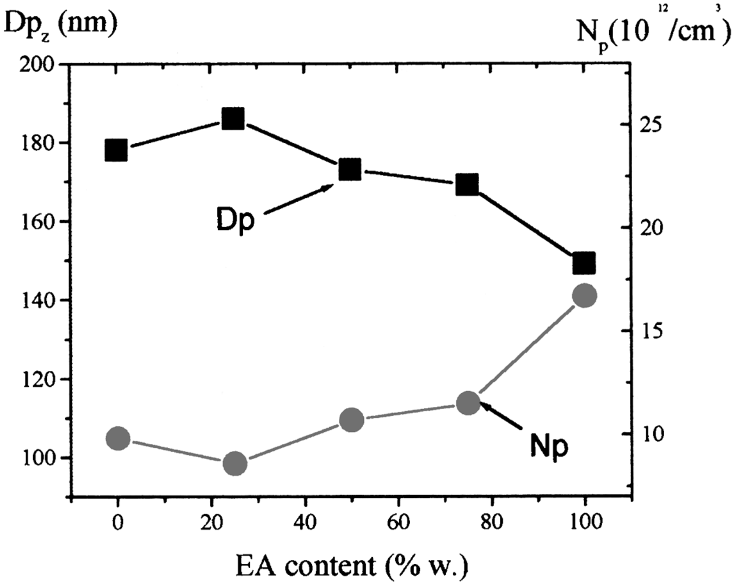


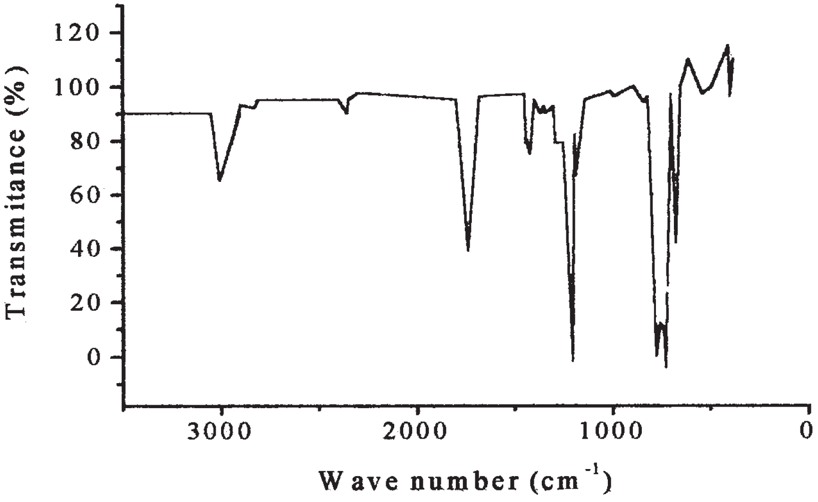
FIGURE 5 Relations between particles diameters and number of particles in the lattices.

corresponding to the carbonyl group (C=O st. 1740 cm^{-1}) and to the ester group (C−OR st 1200 cm^{-1}), which consists of two coupled asymmetric vibrations of −C−CO−OR− and OR−C−C intensely absorbed between 1210–1165 cm^{-1}, were identified. In addition, C−H stretching between 2930–3100 cm^{-1}, the scissoring of the group-CH_2−CO− (δ 1435 cm^{-1}), and the symmetrical bending or "umbrella" of the methyl group at 1450 cm^{-1} were also identified. From the IR spectra, it was determined that in each case, the polymerization was carried out to completion since no characteristic bend for the vinyl group (1648–1638 cm^{-1}) was observed (9,10).

The glass transition of the polymers as a function of monomer content was also investigated (Figure 7). A clear dependence of the Tg on the monomers weight fraction could be established from the classic Fox's equation:

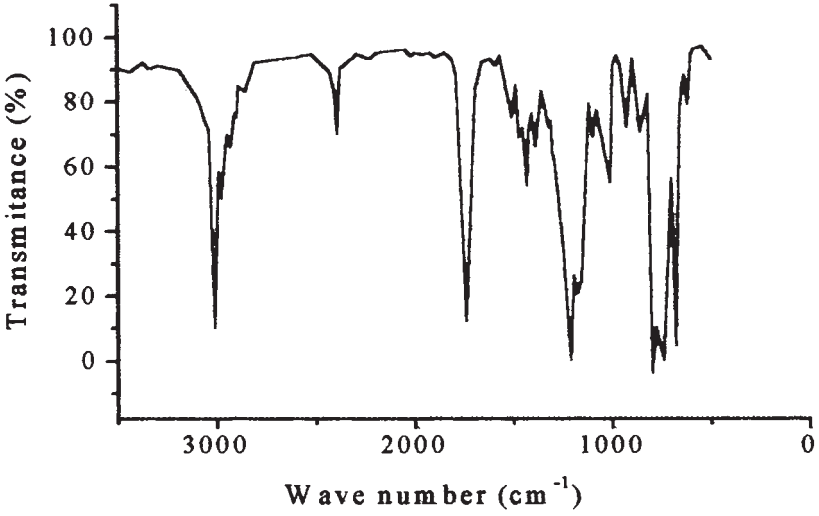
$$\frac{T}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{2}$$

with: Tg_1, Tg_2: homopolymer glass transition temperatures (K),
w_1, w_2: monomer weight fractions.



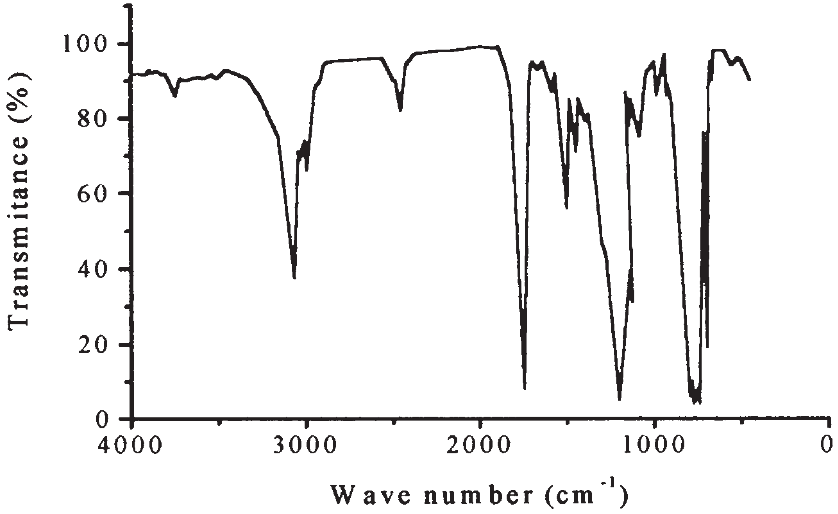
(a)

FIGURE 6a Infrared spectrum of polyethylacrylate prepared at 60°C.



(b)

FIGURE 6b Infrared spectrum of Poly)methylacrylate-co-ethylacrylate (:50/50/ w/w. obtained at 60°C.



(c)

FIGURE 6c Infrared spectrum of polyethylacrylate prepared at 60°C.

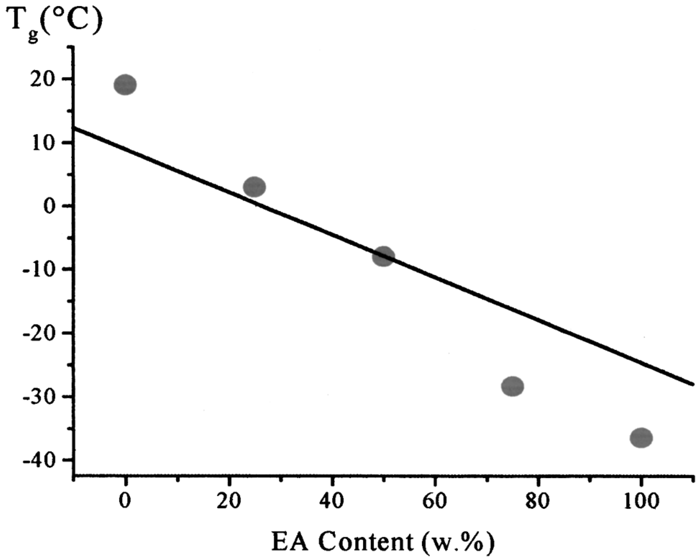


FIGURE 7 Influence of the composition of MeA-EA copolymers on the glass transition temperature.

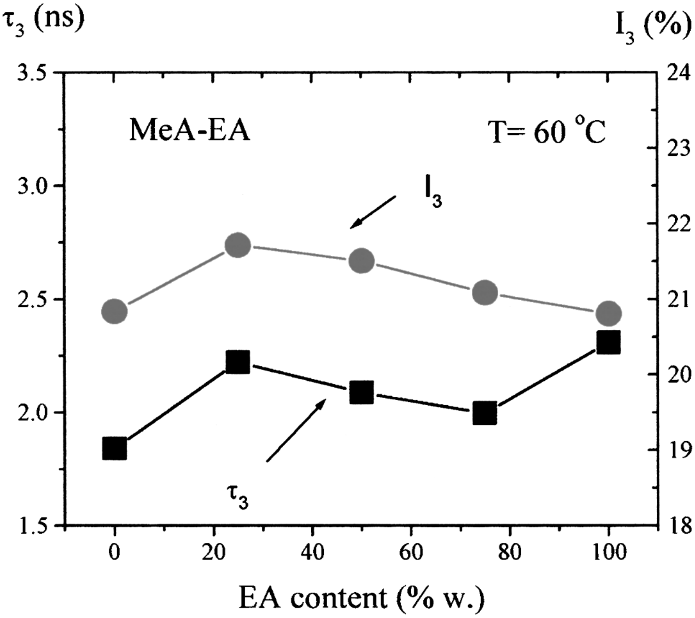


FIGURE 8 Positron annihilation spectroscopy of MeA-EA copolymers as a function the composition.

Positron annihilation spectroscopy (PALS) has been shown to be a useful technique for polymer characterization (11,12). The annihilation parameters of the ortho-positronium (o-Ps) as a function of the copolymer composition are summarized in Figure 8. A continuous increment of the average positronium lifetime (τ_3) with the increment of EA content was observed. This may be explained by the presence of bigger holes constituting the free volume of PEA (with a Tg lower than that of PMeA). It seems that the greatest contribution to the free volume (and to Tg) comes from the increment of the hole size when the EA content is augmented, but this dependence was not found to be linear, as shown in Figure 8.

CONCLUSIONS

A series of latex particles with different ethyl acrylate—methyl acrylate compositions were prepared via polymerization in emulsion using a batch reactor. The temperature was varied and the reaction found to be optimal at 60°C. At higher temperatures, a drastic heat release (auto-acceleration) was observed. In all cases, very stable lattices were obtained, and all the prepared lattices did exhibit very high monodispersity as determined by QELS and confirmed by ETM imaging. Small and uniformly sized particles were probably obtained because of a rapid particle growth and a very fast nucleation reaction. The 100% conversion of the monomers to the polymer was confirmed by IR. PALS measurements show an increment of the free volume within the copolymers with increment of EA content, and the results agree with the measured Tgs. It was also found that PEA has a Tg lower than that of PmeA due to an increase of the free volume present in the material. This phenomenon was also observed when the content of EA increased within the copolymer.

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