

# Morphology–Composition–Processing Relationships in Poly(methyl methacrylate)–Polytriethylene Glycol Dimethacrylate Shrinkage-Controlled Blends

R. Velázquez,<sup>1</sup> I. Ceja,<sup>2</sup> J. Guzmán,<sup>3</sup> V. M. Castaño<sup>1</sup>

<sup>1</sup>Centro de Física Aplicada y Tecnología Avanzada, U.N.A.M., Apartado Postal 1-1010, Santiago de Querétaro, Querétaro 76000, Mexico

<sup>2</sup>Departamento de Física, CUCEI, Universidad de Guadalajara, Guadalajara, Jalisco, Mexico

<sup>3</sup>Instituto de Investigación en Materiales, U.N.A.M., Cd. Universitaria, México, D.F. 04510, Mexico

Received 17 December 2002; accepted 19 May 2003

**ABSTRACT:** An innovative method to control shrinkage in polymer blends, by using *N,N*-dimethyl-*p*-toluidine to produce phase separation in an acrylic system, was applied to synthesize polymer blends from polymethyl methacrylate (PMMA) and polytriethylene glycol dimethacrylate (PTEGDMA). The morphology of several compositions, as analyzed by scanning electron microscopy, reveals microdomains as a function of the specific composition, in contrast to conventional MMA–TEGDMA copolymers synthesized by

thermal decomposition of benzoyl peroxide, used here as reference materials. Micro-Raman and DSC analyses were also carried out to support the electron microscopy results as well. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1254–1260, 2004

**Key words:** blending; morphology; phase separation; curing of polymers; shrinkage

## INTRODUCTION

Much work has been dedicated to control the cure shrinkage typical of polymeric systems, and which represents a serious limitation in a number of industrial, biomedical, and electronics applications. Accordingly, several methods have been proposed either to reduce or to control this consequence of the polymerization reaction.<sup>1–6</sup> Liu and Armeniades<sup>7</sup> proposed a method to control cure shrinkage, which employs *N,N*-dimethyl-*p*-toluidine (DMPT) in the initial step of the polymerization reaction of an acrylic system consisting of a casting syrup and triethylene glycol dimethacrylate (TEGDMA) monomer, the casting syrup being composed of polymethyl methacrylate (PMMA) and methyl methacrylate (MMA) monomer. The reacting system undergoes phase separation and microdomains are produced, and the free volume at the boundaries among microdomains compensates for the cure shrinkage.

On the other hand, many methods have been proposed and tested to synthesize polymer blends, aiming to obtain microstructures with no segregation among the components of the blend or with a domain size as small as possible.

In the present article, a method to control the phase separation in the polymers through the chemical composition of the uncured resin is presented. This chemical composition shows a strong influence on the morphology and size of the domains in the polymer blend and, by combining this effect with the processing conditions during the reaction, microdomains with controlled size were obtained.

## EXPERIMENTAL

The synthesis was carried out using bulk polymerization in open test tubes. The polymerizing system for the polymer blends consisted of a casting syrup made of PMMA and MMA monomer. Three different concentrations of PMMA in the casting syrup were used (i.e., 10, 20, and 30 wt %) and each of the syrups was mixed with TEGDMA monomer in different proportions, from 0 to 100% by weight. The formulation of the uncured resin used for the synthesis of conventional copolymers was a simple mix of MMA and TEGDMA monomers from 0 to 100% by weight. Details about the polymer synthesis and its results were presented in a previous article.<sup>8</sup> Additional reactions, but for all compositions, and both types of polymers were carried out in a dilatometer to determine reaction time and specific volume, both before and after the curing reaction.<sup>8</sup>

The polymer was removed from the test tubes and then saw cut into plates [8 × 20 × 5 mm (width

Correspondence to: V. Castaño (castano@fata.unam.mx).

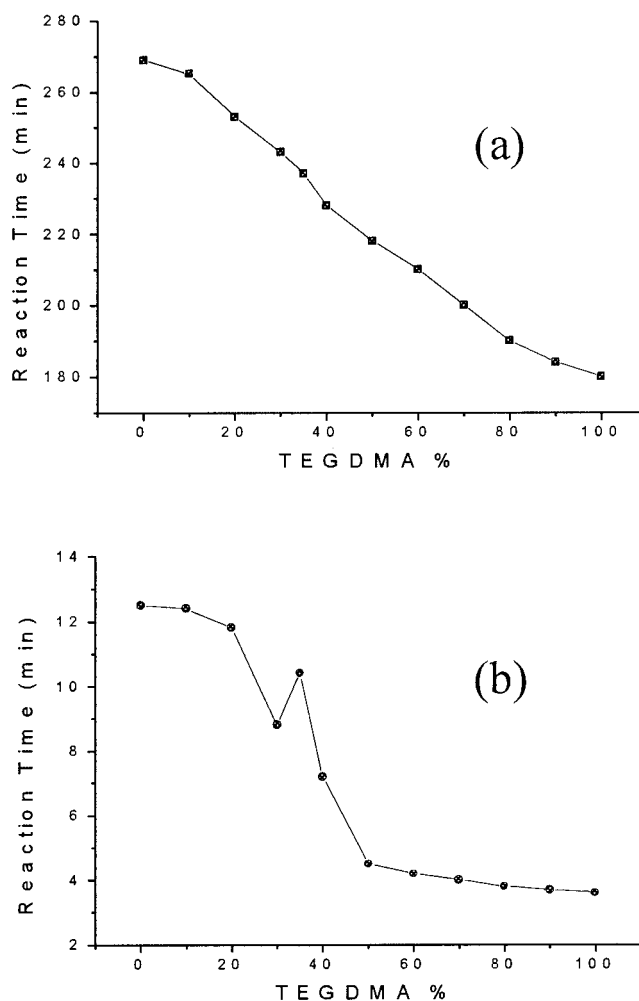
$\times$  length  $\times$  thickness)], which were then immersed into liquid nitrogen until the polymer reached thermal equilibrium with the fluid. Then, the plate was cryo-fractured and one of the fracture surfaces was put in contact with a solvent mixture of acetone and chloroform for a few minutes to clean the surfaces. This solvent mixture removes some of the material localized among the microdomains and helps to enhance the real morphology of the microdomains in the polymer blend. Finally, the sample was attached to a sample holder and coated on the fracture surface with a gold layer by vacuum sputtering. All the images obtained during the observations in the SEM (JEOL 5400 LV; JEOL, Peabody, MA) correspond to secondary electrons. Micro-Raman was carried out in uncoated specimens in a LabRam Dilor machine, according to the procedure reported in the literature.<sup>9</sup> DSC analyses were performed in a Perkin-Elmer DSC 6 apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT).

## RESULTS AND DISCUSSION

When the PMMA/MMA + TEGDMA uncured resins were polymerized inside the dilatometer by DMPT + benzoyl peroxide (BP) mixing, the polymerization reactions were rather fast. The reaction time decreased with the increase of TEGDMA concentration. For example, in the case of composition with casting syrup at 20% of PMMA, the reactions lasted from 12.8 to 3 min, as shown in Figure 1(a). In contrast, the reactions for conventional MMA + TEGDMA copolymers lasted much longer than those for phase-separated polymers, although the reaction time also decreased with the increase of TEGDMA concentration. Figure 1(b) shows the reaction time for conventional copolymer; these reaction times ranged from 270 to 180 min.

These differences in the polymerization rate were obviously produced by the DMPT content, given that this substance promotes the free-radical generation from BP.<sup>10</sup> The mix of BP + DMPT was also used, aiming to initiate polymerization of MMA + TEGDMA, although the reaction did not take place because of the absence of PMMA.

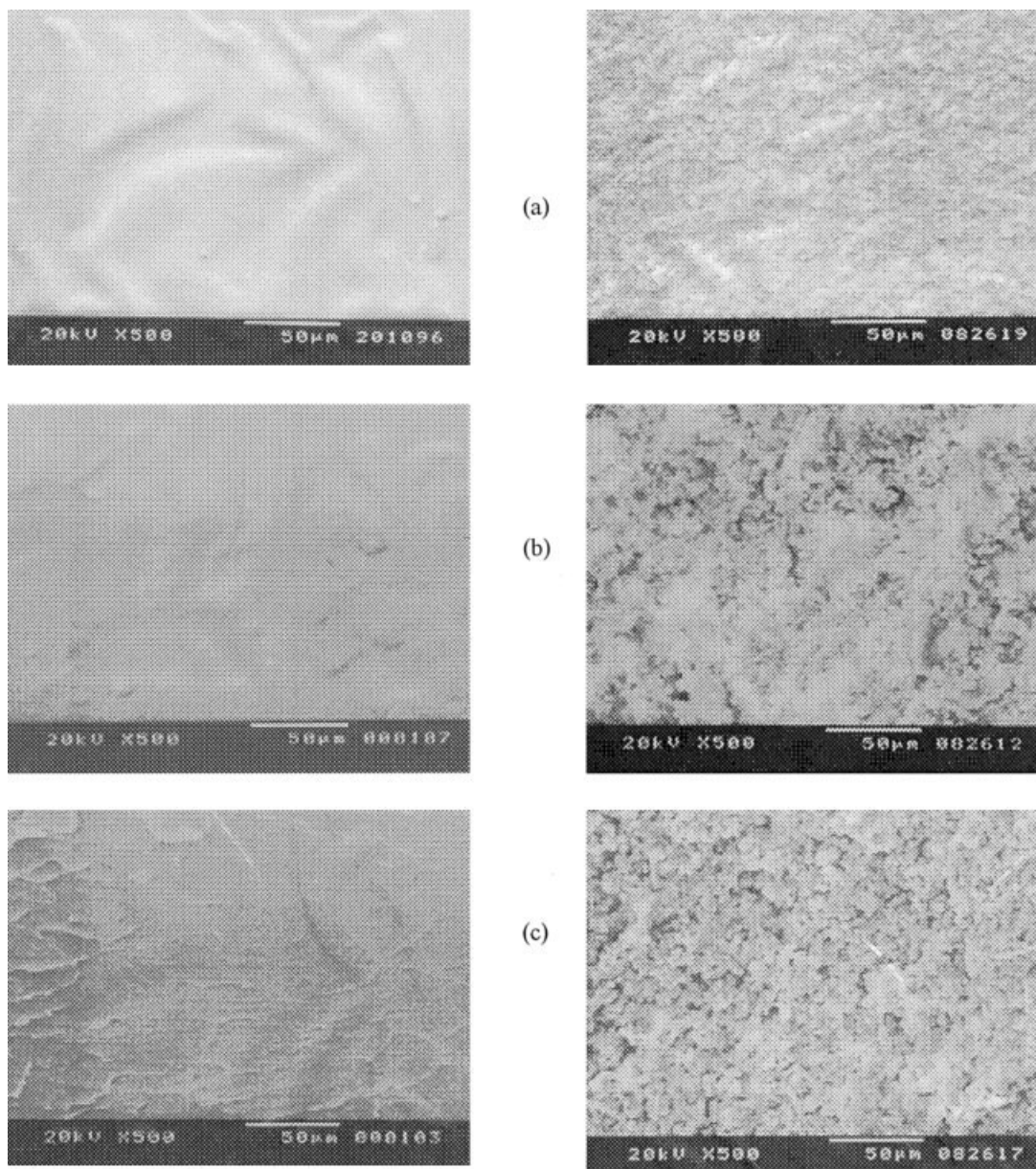
In addition, as observed in the test tubes, the conventional polymers showed a plain and homogeneous surface with no evidence of microcracks, pores, or domains. These morphological characteristics from the conventional polymer can be observed in the micrographs on the left-hand side of Figure 2. These homogeneous surfaces also confirm that the solvent mixture of acetone and chloroform preferentially attacks the interfacial regions. In contrast, phase-separated polymers showed a very irregular surface consisting of small particles randomly distributed within a continuous matrix (i.e., microdomains). The micrographs on the right-hand side of Figure 2 show this



**Figure 1** Reaction time as a function of TEGDMA content for (a) conventional copolymers and (b) phase-separated polymers. Notice the scale of time.

interesting morphology. The differences in the topology in both types of polymers are rather remarkable in spite of their similar chemical composition and reaction conditions. The latter is evidence of the formation of microdomains as a consequence of the phase separation between the PMMA and the PTEGDMA. This separation was produced by the PMMA used previously in the formulation of the casting syrup and also by the use of DMPT.

As for the effect of the PMMA in the casting syrup, when the concentration of the PMMA was increased in the casting syrup, the size of the microdomains also increased. In addition, the shape of the microdomains was sharper when the concentration of the polymer was increased. The micrographs of Figure 3 show the changes in morphology of the polymers when the PMMA concentration was increased. At low PMMA concentrations, the morphology of the polymer blend consisted of small particles embedded in a matrix. The



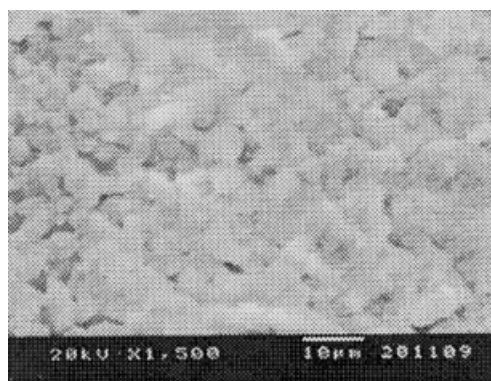
**Figure 2** Comparative micrographs from the sample surfaces of the polymers synthesized by both methods. The conventional copolymer appears in the left column and the phase-separated polymers in the right column. The chemical composition is the same for both types of polymers located in the same line. The PMMA content in the syrup is (a) 10 wt %, (b) 20 wt %, and (c) 30 wt %. All the polymers have 30 wt % of TEGDMA monomer.

small particles are domains of PTEGDMA, according to micro-Raman, and the matrix is composed of PMMA. The average particle size for this case was determined to be  $2.66 \mu\text{m}$ . When the PMMA concentration was increased to 20 wt %, the number of particles and their size also increased considerably, averaging  $4.35 \mu\text{m}$ .

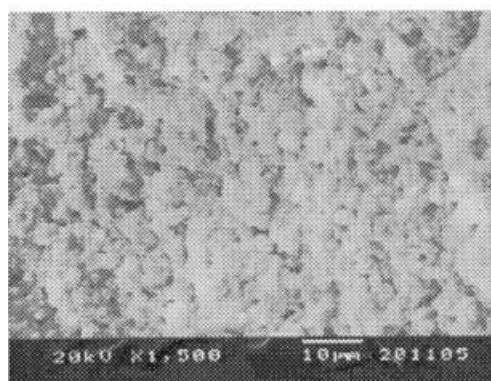
When the PMMA concentration in the syrup was increased to 30 wt %, more spherical particles, with average particle size of  $5.43 \mu\text{m}$ , were found. Figure 4 shows the average particle size distribution as determined by SEM for the different concentrations of PMMA in the casting syrup.

When the TEGDMA content was varied from 0 to 100 wt % (PMMA concentration in the syrup was kept constant at 20% wt) the SEM, at low TEGDMA content, showed that average particle size started to increase when the TEGDMA content was increased to 30 wt % of the monomer. After this concentration, the average particle size decreased when the TEGDMA content was increased. The plot in Figure 5 shows the variation of the average particle size as a function of the TEGDMA content.

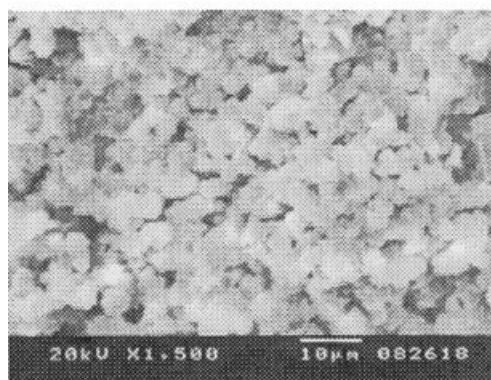
The morphology of the domains was also influenced by the chemical composition. At low TEGDMA contents,



(A)



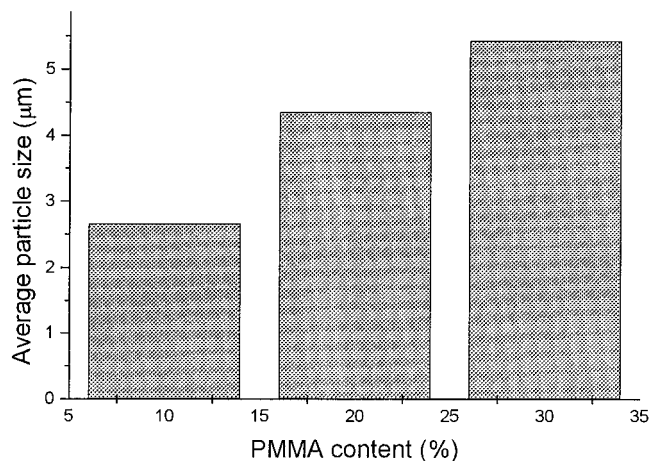
(B)



(C)

**Figure 3** Micrographs from phase-separated polymer samples with different PMMA content in the casting syrup of (A) 10 wt %, (B) 20 wt %, and (C) 30 wt %. All these polymers contain 30 wt % of TEGDMA monomer.

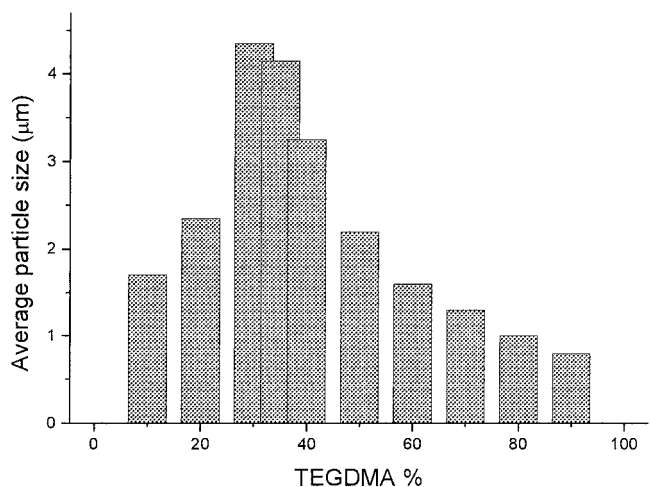
the morphology consisted of small particles of PTEGDMA embedded in a continuous matrix of PMMA, according to micro-Raman analysis. When the TEGDMA concentration was increased, not only was the size of the PTEGDMA domains increased, but also the continuous matrix of PMMA began to transform into particles. In polymers with compositions of 30 and 35 wt % of TEGDMA, only particles could be observed, and the contin-



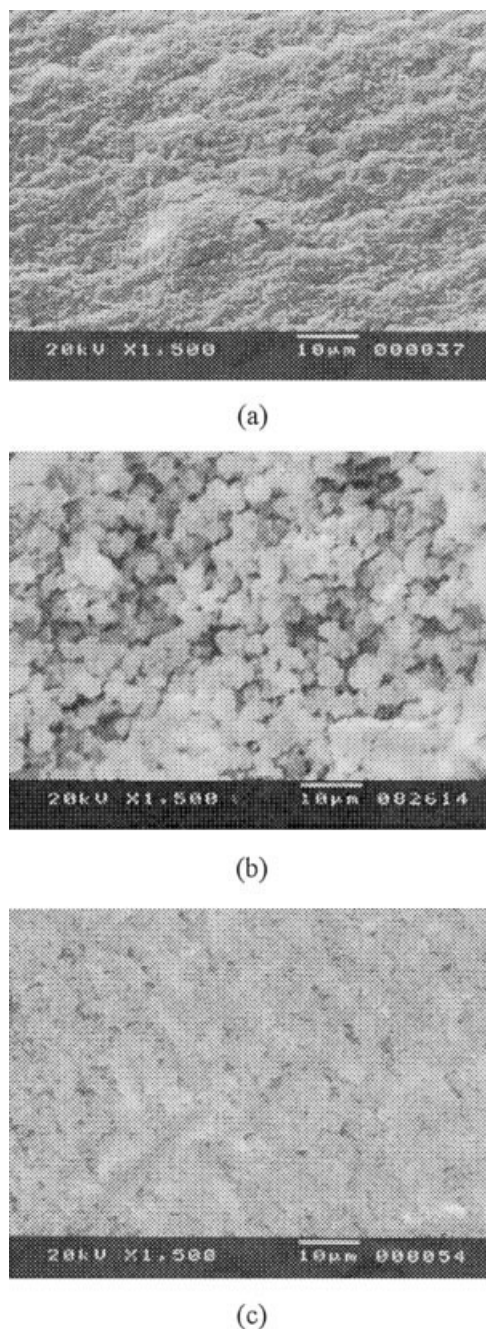
**Figure 4** Variation of the average particle size as a function of the PMMA content in the casting syrup. In all cases the TEGDMA content in the reacting mixtures was 30 wt %.

uous matrix could not be observed, as shown in Figure 6(b). Finally, when the TEGDMA content was increased at high concentration of the monomer, the morphology changed again and a phase inversion occurred. Now, the microstructure of the polymer consisted of particles immersed in a matrix, although the particles consisted of PMMA and the matrix consisted of PMMA. Figure 6 shows the variation of the morphology as a function of the TEGDMA concentration in the formulation of the reacting mixture. A similar behavior was observed for the polymer with 10 and 30 wt % of PMMA in the casting syrup.

The specific volume for all the polymers and uncured resins was determined by dilatometry. The change in the specific volume was calculated for both types of polymers by subtracting the specific volume of the polymer from the specific volume of its corre-



**Figure 5** Variation of the average particle size as a function of the TEGDMA content in the reacting mixture.



**Figure 6** Micrographs from phase-separated polymer samples with different TEGDMA contents of (a) 10 wt %, (b) 30 wt %, and (c) 70 wt %. All these polymers contain casting syrup in a 20 wt % concentration of PMMA.

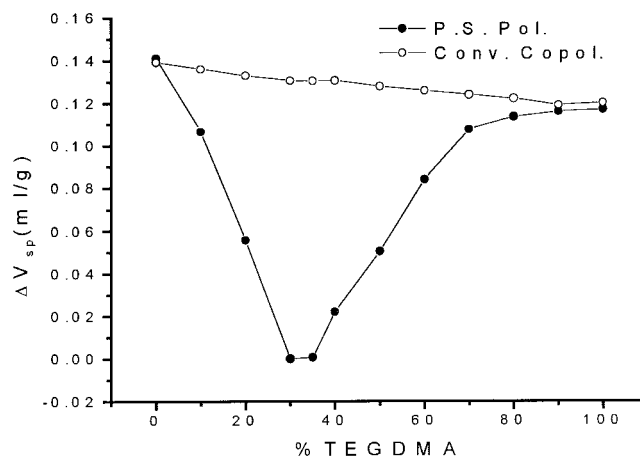
sponding uncured resin. The results for phase-separated polymer containing 20 wt % of PMMA in the syrup and conventional copolymer are shown in Figure 7. The change in the specific volume ( $\Delta V_{sp}$ ) for the conventional copolymers was very consistent. The  $\Delta V_{sp}$  decreased with the increase of TEGDMA. Conventional copolymers had a considerable volume shrinkage, and the TEGDMA content contributes to

reduction of this shrinkage. On the other hand, phase-separated polymers had a variable  $\Delta V_{sp}$ . At the beginning, the volume shrinkage decreased substantially with the increase of TEGDMA monomer up to 30 wt %. From a content of 35%,  $\Delta V_{sp}$  began to increase when TEGDMA concentration was increased, and finally (in contents of 90 and 100 wt %), the  $\Delta V_{sp}$  values for phase-separated polymers were very similar to those of conventional copolymers.

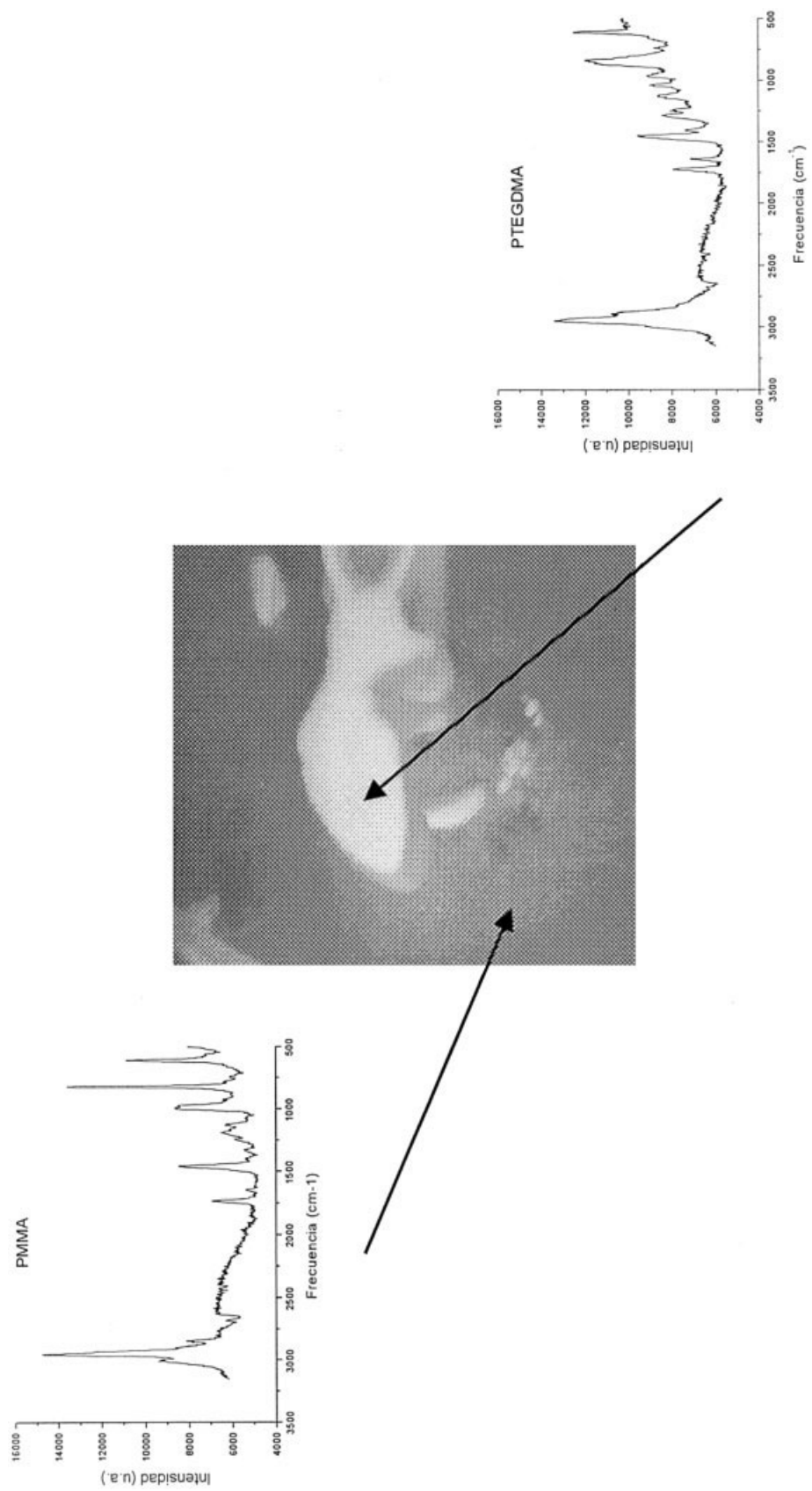
The phase-separated polymers with TEGDMA concentration of 30 and 35 wt % are shrinkage-free polymers. This last result is consistent with the variation of the average particle size as a function of the TEGDMA content shown in Figure 5. The largest average particle sizes determined were for the TEGDMA contents of 30 and 35 wt %. These larger particle sizes contribute to control of volume shrinkage, and a larger particle size also produces a higher interfacial volume among particles; this volume in turn is one of the main factors that contribute to reduction of volume shrinkage.

Figure 8 shows an optical microscopy photograph from one of the microdomains embedded in a matrix. The results from the microanalysis of those polymer blends showed that the microdomain consisted of PTEGDMA and the matrix consisted of PMMA. Similar analyses were performed in polymer blends consisting of 20 wt % of syrup (20 wt % PMMA) and 80% of TEGDMA monomer, and the results showed that the microdomains consisted of PMMA and the matrix consisted of PTEGDMA.

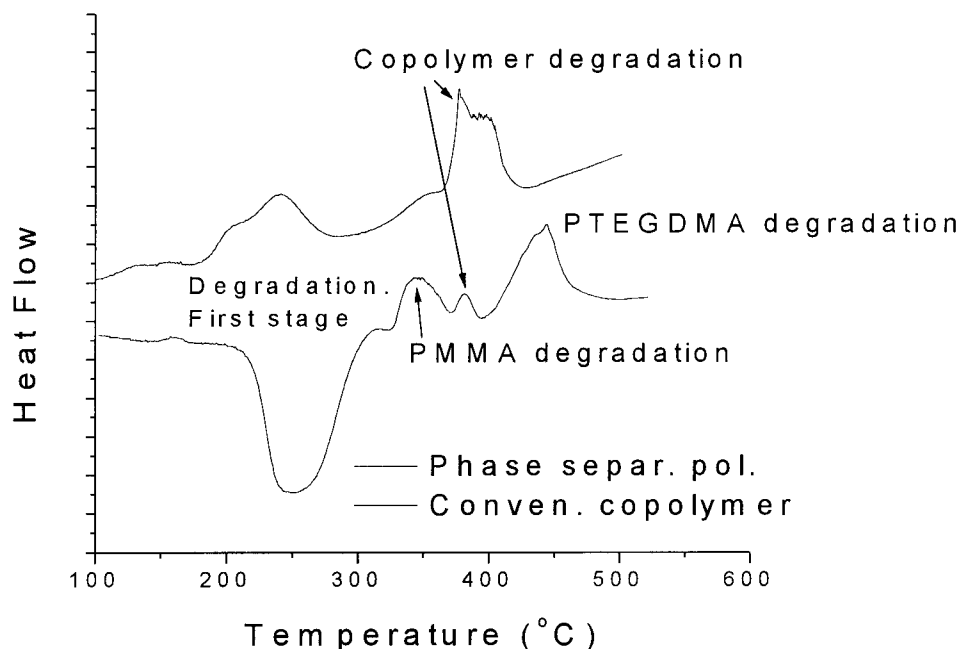
Figure 9 shows the DSC thermographs for both types of polymers. The conventional copolymer presented one endothermic peak at 200°C and exothermic peaks at 250 and 378°C, which could be the result of different stages of the copolymer degradation. The phase-separated polymer showed a very broad endo-



**Figure 7**  $\Delta V_{sp}$  as a function of TEGDMA concentration for conventional and phase-separated polymers.  $\Delta V_{sp} = \Delta V_{sp}$  (uncured) -  $\Delta V_{sp}$  (polymer).



**Figure 8** Optical microscopy photograph of a phase-separated polymer sample containing 65 wt % of casting syrup (20 wt % PMMA) and 25% TEGDMA. The micro-Raman analyses determined that the matrix consisted of PMMA and the microdomains consisted of PTEGDMA. The sites analyzed in the sample are indicated by arrows in the photograph.



**Figure 9** Thermograms obtained from samples of the two types of polymers. Both types of polymers have a composition of 65 wt % of casting syrup (20 wt % of PMMA) and 35 wt % of TEGDMA. The square region in the bottom-right side of the figure is a magnification of the thermograms showing the glass-transition temperatures ( $T_g$ ) determined for each type of polymer.

thermic band at 250°C and three peaks at 345, 380, and 440°C. The first peaks coincide with those observed in a thermogram for the final degradation of pure PMMA. The second peak is very close to that obtained for the final degradation of conventional copolymer and, possibly, small regions of MMA-TEGDMA copolymer are present in the phase-separated copolymer. The last peak observed for this type of polymer is very similar to that corresponding to the final degradation of pure PTEGDMA.

## CONCLUSIONS

From the reaction time results it was determined that TEGDMA monomer is more reactive than MMA monomer. Then, when the faster polymerization (by DMPT + BPO) was carried out, PTEGDMA microdomains were initially produced and these domains interact with the PMMA previously contained in the casting syrup, and phase separation started to occur. The slower polymerization (by BPO only) and the absence of PMMA prevent that phase separation from occurring.

The phase-separated polymers showed a microstructure composed of particles that are microdomains of different compositions, some of which were composed of PTEGDMA and others composed of PMMA. A strong influence of the PMMA and PTEGDMA concentration in the reacting mixtures on the size, amount, and morphology of microdomains was observed. The increase of average size and number of particles and their corre-

sponding interfacial volume contribute to reduction of volume shrinkage. In this way, it was possible to control the microstructure and final volume of the polymers by conveniently modifying the chemical composition of the reacting mixtures and the agitation conditions during the curing reaction.

The authors acknowledge Dr. Sergio Jimenez S. and M. en C. Francisco Rodríguez M. for their assistance in the micro-Raman analyses; and M. en C. Jacqueline Cañetas, Ing. Domingo Rangel M., and Edgar Méndez M. for their technical support.

## References

1. Haque, E.; Armeniades, C. D. In: Proceedings of the 43rd Technical Conference of Society of Plastic Engineers, 1985; pp. 1239–1241.
2. Haque, E.; Armeniades, C. D. In: Proceedings of the 44th Technical Conference of Society of Plastic Engineers, 1986; pp. 1296–1301.
3. Bailey, W. J. *J Elastoplast* 1973, 5, 142.
4. Atkins, K. E. *Low-Profile Behavior Polymer Blends*, Vol. 2; Academic Press: New York, 1978; pp. 391–414.
5. Hsu, C. P.; Lee, L. J. *Plastic Eng* 1989, November, 45.
6. Okada, T. Konaka, T. In: Proceedings of the 3rd International Congress on Polymers in Concrete, Nihon University, 1982; pp. 1, 447–461.
7. Liu, C.; Armeniades, C. D. In: Proceedings of the 47th Technical Conference of Society of Plastic Engineers, 1990; pp. 588–590.
8. Velázquez, R.; Sánchez, F.; Yañes, R.; Castaño, V. M. *J Appl Polym Sci* 2000, 78, 586.
9. Jiménez, S. *Microelectron J* 2000, 31, 419.
10. Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*; Wiley-Interscience: New York, 1978; p. 10.