Polymer Bulletin 60, 417–423 (2008)
DOI 10.1007/s00289-007-0882-6

Polymer Bulletin

A rubber-modified thermoplastic where the morphology produced by phase-separation induced by polymerization disappears at high conversions

Ezequiel R. Soulé, Guillermo E. Eliçabe, Roberto J.J. Williams (✉)

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and
National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina
E-mail: williams@fi.mdp.edu.ar; Fax: +54-223-4810046

Received: 10 September 2007 / Revised version: 29 October 2007 / Accepted: 16 December 2007

Summary

An unexpected experimental finding is reported where the primary morphology developed during polymerization-induced phase separation in a rubber-modified thermoplastic practically disappears at high conversions. This process was evidenced by light scattering (LS) and scanning electron microscopy (SEM) for a particular composition of solutions of polyisobutylene oligomers (PIB) in isobornylmethacrylate (IBoMA), during the free-radical polymerization of the monomer. The primary phase separation produced a dispersion of domains rich in PIB containing significant amounts of the monomer (IBoMA). Polymerization of the monomer in these domains occurred at high overall conversions producing the filling of dispersed domains with a PIBoMA-PIB blend that could not be distinguished from the matrix. Under these conditions the final material had the appearance of a homogeneous blend.

Introduction

A phase separation process might take place when a polymerization is carried out employing a solution of a suitable modifier (e.g., rubber, thermoplastic polymer, liquid crystal) in the starting monomers. Thermodynamic factors that drive the polymerization-induced phase separation have been extensively discussed in the literature [1-5]. The main factor is the increase in the average size of reaction products and the corresponding decrease in the entropy of mixing. Secondary factors are the variation of the interaction parameter as a result of changes in the chemical structures, and elastic effects when a network is formed. Morphologies generated by this process depend on the initial composition and on the competition between the kinetics of polymerization and phase separation.

We have recently analyzed the phase separation process that occurs in solutions of polyisobutylene oligomers (PIB) in isobornylmethacrylate (IBoMA), during the free-radical polymerization of the monomer [6]. Under the conditions investigated, a dispersion of PIB-rich droplets was generated during polymerization. The average size of these domains increased with conversion attaining a plateau value. Then, we decided to investigate the effect of a prolonged heating at the polymerization temperature on the morphologies generated. In most cases no significant variation of morphologies was observed. But one set of blends exhibited a completely unexpected behaviour: at the end of the heating dispersed domains had almost disappeared and the material resembled a homogeneous blend. This curious behaviour has not been previously reported in the literature and will be analyzed in the present communication.

Experimental

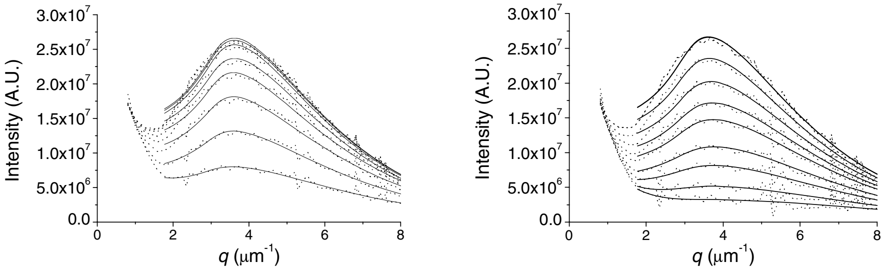
The polymerization of a solution containing 15 wt % or 30 wt % polyisobutylene (PIB, YPF-Repsol, M_n = 1339 g/mol, M_w = 3035 g/mol) in isobornyl methacrylate (IBoMA, Aldrich), was performed at 80 °C in the presence of benzoyl peroxide (BPO, Akzo-Nobel, 2 wt % in the mixture with IBoMA).

Polymerization-induced phase separation was followed in situ by light scattering (LS) using an experimental set up described elsewhere [6]. In order to transform polymerization times into monomer conversions we used conversion vs. time curves obtained for by differential scanning calorimetry operating in the isothermal mode (DSC, Pyris 1, Perkin-Elmer). The cloud-point conversion determined independently was used to refer the time scale of LS to the conversion vs. time after phase separation obtained by DSC. This procedure was used up to a conversion equal to 0.85, where the polymerization appeared to be practically arrested as inferred from the return of the isothermal DSC signal to the baseline. The slow increase in conversion after this point was followed measuring the evolution of the residual reaction heat in DSC scans (10°C/min).

SEM micrographs of fracture surfaces coated with a fine gold layer were obtained using a Jeol JSM 6460 LV device.

Results and Discussion

Figure 1a shows LS spectra in the 0.506 – 0.788 conversion range while Figure 1b shows LS spectra in the 0.801 – 0.93 conversion range, for the blend with 15 wt % PIB cured at 80°C.



(a) **(b)**

Figure 1. Light scattering spectra plotted as intensity (arbitrary units) as a function of the modulus of the scattering vector q. Points are experimental results and the curves represent the fitting obtained with Pedersen's model. In (a) the intensity increases with monomer conversion (0.506, 0.548, 0.585, 0.617, 0,673, 0.719, 0.757, 0,788); in (b) the intensity decreases with monomer conversion (0.801, 0.854, 0.856, 0.858, 0.859, 0.861, 0.865, 0.88, 0.93)

Starting at the cloud-point conversion ($p_{cp} = 0.41$), a peak in the intensity (I) vs. scattering vector (q) spectra was generated with a maximum increasing with conversion up to a value close to 0.80 where vitrification of the matrix took place. For higher conversions the intensity of the peak began to decrease and practically disappeared for $p = 0.93$ (Figure 1b). The increasing period of the LS signal took place during about 4 min while the decreasing period was gradually observed during the following 130 min at 80 °C (in a time scale the intensity of the peak increased at a fast rate and decreased at a slow rate).

The disappearance of the scattering peak in systems undergoing a polymerization-induced phase separation has already been reported in the literature and ascribed to the matching of refractive indices of both phases [7], or to a broadening of the distribution of dispersed particles [8]. We will show that in our case the decrease in the scattered intensity is associated to the disappearance of the morphology initially formed.

Particle-size distributions were obtained from LS spectra, using a model proposed by Pedersen [9], as described in a previous publication [6]. Full curves shown in Figure 1 indicate the excellent fitting of I vs. q curves obtained with this model. The evolution of the predicted average radius of dispersed-phase domains as a function of conversion is shown in Figure 2. The average radius of the population increased with conversion attaining a limiting value in a conversion range comprised between 0.80 and 0.85. A sharp decrease in the average radius was predicted by applying Pedersen's model at conversions higher than 0.85.

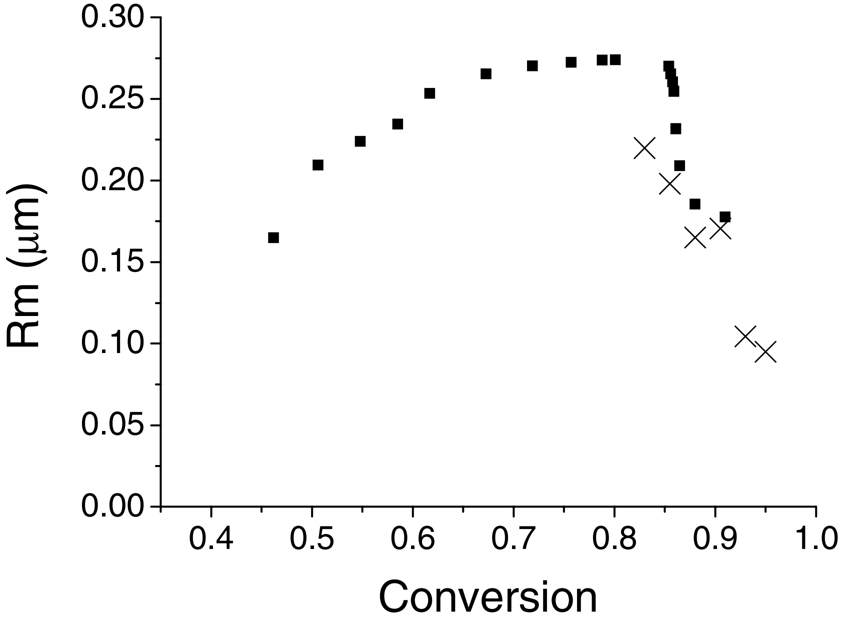
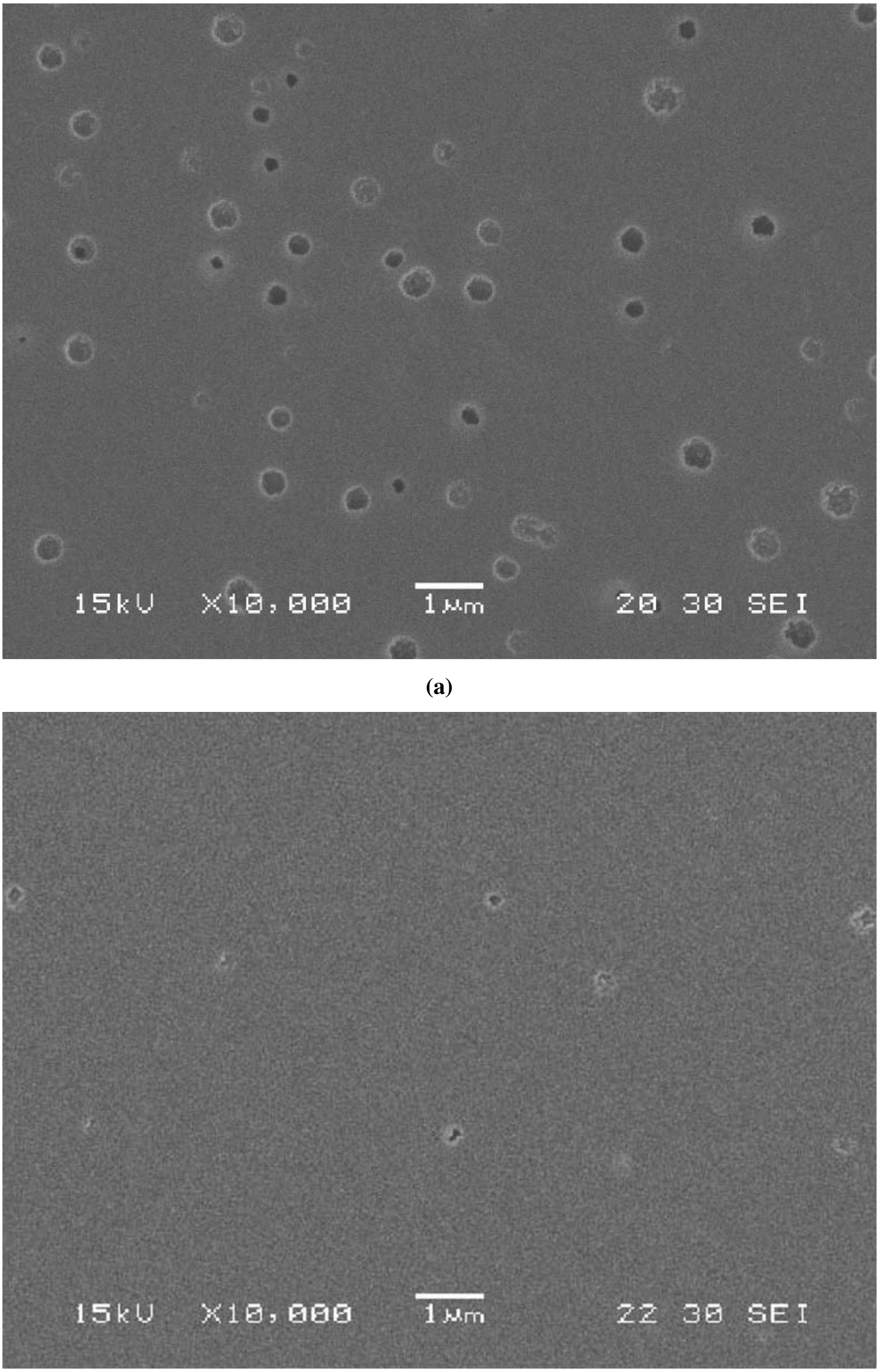


Figure 2. Average radius of dispersed-phase droplets as a function of the monomer conversion for the blend with 15 wt % PIB (full symbols are values predicted from the fitting of LS curves using Pedersen's model; crosses are values determined from SEM images)

Figure 3 shows SEM images of the blend containing 15 wt % PIB for conversions equal to 0.85 and 0.95.



(a)

(b)

Figure 3. SEM micrographs of the blend containing 15 wt % PIB obtained at different monomer conversions: (a) 0.85, (b) 0.95

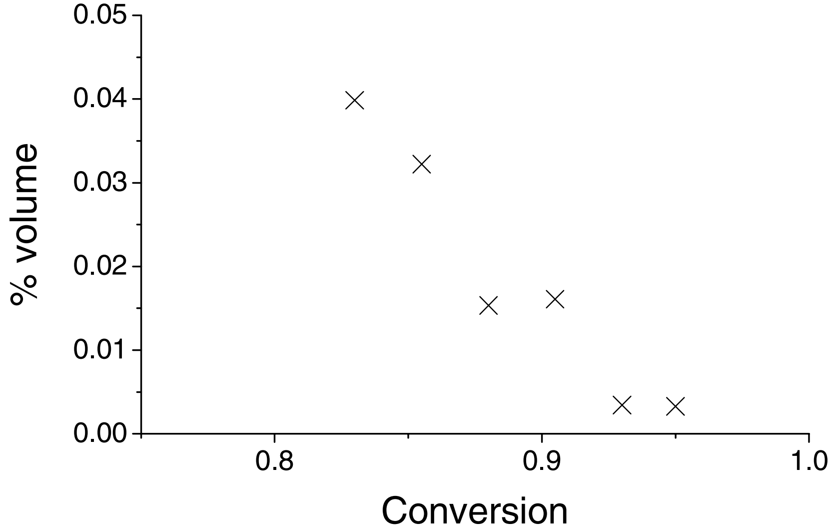


Figure 4. Evolution of the volume fraction of dispersed phase as a function of conversion

Clearly, there is a decrease in the concentration and size of dispersed-phase domains in the high conversion range. The average radius and volume fraction of dispersed-phase domains were estimated from SEM images following usual procedures [10]. The evolution of the average radius is plotted in Figure 2 showing a reasonable agreement with LS data up to conversions where reliable information could be obtained from the latter technique. The decrease in the volume fraction of dispersed phase is plotted in Figure 4.

The reason of the decrease in the size and concentration of dispersed domains was ascribed to a secondary phase separation taking place at high conversions. At the cloud-point conversion dispersed domains are constituted by a blend rich in PIB but containing a significant fraction of IBoMA [6]. The monomer present in dispersed domains undergoes a slow polymerization that continues after vitrification of the matrix [11], as shown by the evolution of DSC thermograms (Figure 5).

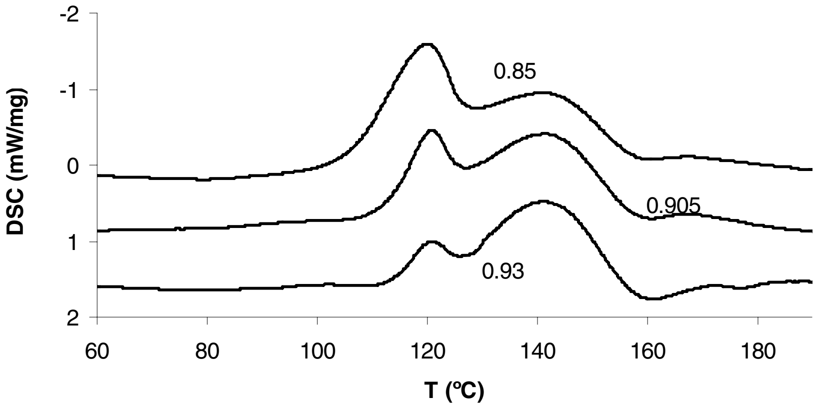


Figure 5. DSC scans showing the polymerization of the residual monomer in samples previously reacted to the indicated overall conversions

The residual heat is composed of two well-defined peaks. While the first peak decreased significantly with conversion the second one experienced only a small decrease. With this evidence, the first peak was assigned to the polymerization of residual monomer still present in dispersed domains, and the second peak was ascribed to the polymerization of residual monomer present in the matrix after its devitrification at about 120ºC.

Polymerization of IBoMA in dispersed domains generates PIBoMA that is not compatible with PIB. Therefore, a secondary phase separation is expected inside the dispersed droplets. The PIBoMa-rich phase containing a fraction of dissolved PIB merges with the matrix erasing the contours of dispersed domains. Only a very small fraction of tiny droplets of PIB remains dispersed in the matrix at the end of this process (Figure 3b).

In order to visualize better this secondary phase separation, a blend containing 30 wt % PIB was analyzed. Figure 6 shows SEM images of this blend at a high overall conversion.

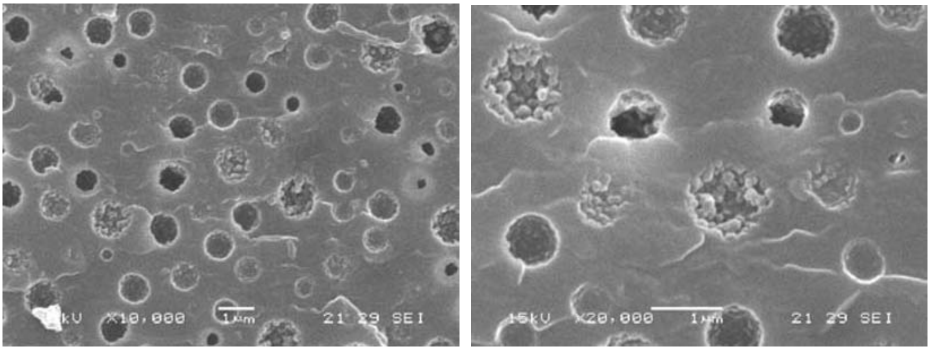


Figure 6. SEM micrographs of a blend containing 30 wt % PIB at on overall conversion higher than 0.95 (two different magnifications)

The presence of a secondary phase separation taking place in dispersed domains is evidenced in SEM micrographs. PIBoMA-rich domains can be clearly distinguished. In the high-magnification image a partial merging of these domains with the matrix can be observed that partially erases the spherical contour of some of the particles. Due to the high amount of PIB in the initial blend, this process took place only to a limited extent. But for the blend containing 15 wt % PIB an almost complete disappearance of dispersed domains was produced by secondary phase separation followed by the merging of the new phase with the matrix.

Conclusions

We showed that the primary morphology developed at low conversions during a polymerization-induced phase separation in a particular rubber-modified thermoplastic, almost disappeared at high conversions. This unusual behaviour was explained by the presence of a secondary phase separation inside dispersed domains that generated a new blend rich in the thermoplastic that merged with the matrix. At the end of this process a small fraction of tiny domains containing rubber remained in the final material.

Acknowledgements. We acknowledge the financial support of the following institutions of Argentina: University of Mar del Plata, National Research Council (CONICET), and National Agency for the Promotion of Science and Technology (ANPCyT).

References

1. Williams RJJ, Borrajo J, Adabbo HE, Rojas AJ (1984) In: Rubber-Modified Thermoset Resins. Riew CK, Gillham JK, editors. Adv Chem Ser 208, American Chemical Society, Washington DC, p.195-213
2. Inoue T (1995) Prog Polym Sci 20:119
3. Clarke N, McLeish TCB, Jenkins SD (1995) Macromolecules 28:4650
4. Williams RJJ, Rozenberg BA, Pascault JP (1997) Adv Polym Sci 128:95
5. Eliçabe GE, Larrondo HA, Williams RJJ (1998) Macromolecules 31:8173
6. Soulé ER, Eliçabe GE, Borrajo J, Williams RJJ (2007) Ind Eng Chem Res in press (web release date: 06-Mar-2007; DOI: 10.1021/ie061567c)
7. Kim BS, Chiba T, Inoue T (1995) Polymer 36:67
8. Yang Y, Fujiwara H, Chiba T, Inoue T (1998) Polymer 39:2745
9. Pedersen JS (1994) J App Cryst 27:595
10. Verchère D, Pascault JP, Sautereau H, Moschiar SM, Riccardi CC, Williams, RJJ (1991) J Appl Polym Sci 42:701
11. Soulé ER, Borrajo J, Williams RJJ (2005) Macromolecules 38:5987