Reactive Compatibilization of Poly(butylene terephthalate)/ Low-Density Polyethylene and Poly(butylene terephthalate)/ Ethylene Propylene Diene Rubber Blends with a Bismaleimide

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ABSTRACT: The reactive compatibilization effect of a small molecule, bismaleimide (BMI), on poly(butylene terephthalate) (PBT)/low-density polyethylene (LDPE) and PBT/ethylene propylene diene (EPDM) rubber blends were investigated. All the blends were prepared by melt blending in the mixing chamber of a Haake Rheocord. The particle size of dispersed phase was reduced by >ten times by adding 1.2 wt % of BMI as observed with scanning electron microscopy. The torque-time curve recorded during mixing showed that the addition of BMI leads to a significant increase in the viscosity of PBT, LDPE, EPDM, and the blends. This indicates that a chemical reaction has taken place. It was confirmed that free radicals are involved in the reactions because the addition of a stabilizer to the blends has removed all the compatibilizing effect, and the torque-time curve does not show any increase in viscosity. A possible mechanism of compatibilization is proposed. The shear forces during melt mixing cause the rupture of chemical bond in the polymers, which form macroradicals of PBT, LDPE, or EPDM. These macroradicals react with BMI to form PBT-BMI-LDPE or PBT-BMI-EPDM copolymers. These *in situ*-formed copolymers act as compatibilizers to give a significant refinement of the blend morphology. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2049-2057, 1999

Key words: polymer blends; stress reaction; bismaleimide; compatibilization

INTRODUCTION

The interface in a polymer blend is important both in the preparation of the blend and in determining its ultimate properties. For making rubber-toughened thermoplastics, the greatest toughness is achieved when the interparticle distance is smaller than a critical value,¹ depending on how the fracture energy is dissipated. During mechanical melt

* Present address: Department of Chemical Engineering, Jilin Institute of Technology, Changchun 130012, China. Journal of Applied Polymer Science, Vol. 71, 2049–2057 (1999) mixing of two immiscible polymers, the break up of the drops of one polymer within a matrix of the other is determined in part by the interfacial tension.² Interfacial agents, such as di-block copolymers with blocks being identical or miscible with a component of the blend, are known to increase the interfacial adhesion (i.e., reduce the interfacial tension) and hence are expected to increase the degree of dispersion in blends. For example, polystyrene (PS)-hydrogenated polybutadiene block copolymer can be used as a compatibilizer for low-density polyethylene (LDPE)/PS blends.^{3–5} The block or grafted copolymers are generally prepared separately and introduced in low concentrations to the melt-mixing system. An alternative way of compatibilizing im-

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miscible blends is to create these block or graft copolymers *in situ* by adding a suitable functionalized polymer that can react with blend components by using their inherent chemical reactivity based on end-capping or grafting reactions. Examples include using maleic anhydride-functionalized polymer to blend with polyamides,⁶⁻⁹ styrenic copolymers containing oxazoline groups to blend with polyamides,^{10,11} or carboxylated polyolefines¹² and styrene-acrylonitrile-glycidyl methacrylate copolymer as compatibilizers for poly(butylene terephthalate) (PBT)/acrylonitrile-butadiene-styrene copolymer (ABS) blends.¹³ However, block copolymers or reactive functionalized polymer usually require a separate preparation step, and certain copolymers are difficult to obtain. The price of the blends are, hence, much higher than the sum of the parent polymers due to the high cost of a compatibilizer. Therefore, it would be a great advantage simply to use a small molecule compound as a compatibilizer.

During melt-blending, polymers are subjected to shear deformation and high temperature. Under these conditions, stress-induced reactions must be considered.^{14,15} With increasing molecular weight, the conversion of the mechanical energy applied to a polymer is shifted increasingly from viscous to elastic (i.e., from thermal dissipation toward molecular energy storage). This energy storage leads ultimately to the rupture of chemical bonds. Macroradicals are generated, and various free radical reactions could be initiated. At high viscosity, bonds are ruptured more efficiently by shear, because the stresses are higher, whereas polymers of low molecular weight are likely to relax so fast that they can escape stress reactions. The rate and extent of the reaction depend on the chemical nature of the polymer, as well as on reaction conditions (e.g., temperature, stress and equipment). In the rubber industry, stress reactions are used in mastication of raw rubber. The shear stress applied by a two-roll mill leads to chain degradation and transforms the raw rubber into a coherent mass. In the plastic processing industries, stress reaction is usually unfavorable, because it causes degradation of the polymer chains, which leads to reduced mechanical strength of the products.

In some applications, stress reactions are favorable. Some copolymers are produced by the method of mechanical synthesis.¹⁴ When different polymers are blended in internal mixers or extruders, polymer chains can be ruptured by mechanical scission and macroradicals generated. These macroradicals can have a series of further reactions. They can reform to the origin polymer by recombination, and they also can form a copolymer by cross-combination. If a monomer is added to the system, the macroradical can initiate polymerization to form a block copolymer.

In this article, we will report the reactive compatibilization of PBT/LDPE and PBT/ethylene propylene diene (EPDM) blends by using a small molecule, bismaleimide (BMI), and will propose a possible compatibilizing mechanism based on stress reactions.

EXPERIMENTAL

Materials

PBT, Arnite T06 204, was provided by Akzo (Arnhem, The Netherlands). Polyethylene (PE) and polypropylene (PP) were from Exxon Chemicals, Belgium. The grade code of PE is LD1008BW. PS, grade 303, was from Huntsman. The ethylene propylene terpolymer (EPDM), Keltan 720, was from DSM Holland. 1,1'-(methylenedi-4,1-phenylene)-bismaleimide, 95%, was supplied by Aldrich (Milwaukee, WI). The stabilizer, Irganox 1010, was donated by Ciba-Geigy Additives. Its chemical structure is pentaerythrityl-tetrabis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate).

Melt-Blending

PBT was dried in a vacuum oven at 120°C for 24 h before use. Blends were prepared using a Haake Rheomix 600 driven by a Haake Rheocord 90. The volume of the mixing chamber was \sim 60 mL. Sixty grams of blends were prepared per operation. These blends contained 50 g of PBT as a matrix and 10 g of the minor component as the dispersed phase. The speed of the mixer was 130 rpm, and the set temperature was 233°C, but the actual temperature in the mixer is increasing during the blending due to viscous heating. In some cases, it reached 255°C at the end of the process. PBT was introduced into the mixer first. After it was completely melted, the other components were added after a predesigned sequence. A curve of torque versus time was recorded during the mixing process.

Morphology Observation

A scanning electron microscope (SEM), Cambridge Stereoscan 360, was used to observe the morphology of the blends. The materials were hot-pressed and sliced into strips, precracked by a razor blade at room temperature, and then fractured at the cryogenic temperature. For easier observation, some specimens were etched with boiling toluene, which dissolves the dispersed phase and leaves holes.

RESULTS AND DISCUSSION

The SEM micrographs in Figure 1 show the effect of adding BMI on the morphology of PBT/LDPE. PBT/EPDM, PBT/PP, and PBT/PS blends. The mixing time for all the blends was 10 min; BMI was added immediately after the main component had been compounded. Comparing SEM micrograph of sample A with B, and C with D, shows that the PBT/LDPE and PBT/EPDM blends are highly incompatible with a very large particle size for the dispersed phase, $\sim 15 \ \mu m$ and 10 μm for LDPE and EPDM, respectively. However, by adding 1.2 wt % of BMI to the same blend, the particle size were reduced to $\sim 2.0 \ \mu m$ and 1.5 μm , respectively. This indicates clearly that BMI is a very effective compatibilizer. Its efficiency of compatibilization is comparable with or even higher than conventional polymeric compatibilizers, such as block copolymers or reactive functionalized polymers.¹⁶

Micrographs of samples E–H in Figure 1 show that the addition of BMI does not improve the dispersion of PP or PS in PBT matrix, which indicates that BMI does not have any compatibilizing effect in these systems.

Although these facts show that BMI is a highly efficient compatibilizer for PBT/LDPE and PBT/ EPDM blends, it raises two questions: (1) What is the mechanism for the compatibilization? (2) Why is it effective in some systems and not in others? To answer these questions, the reactivity of BMI should be reviewed.

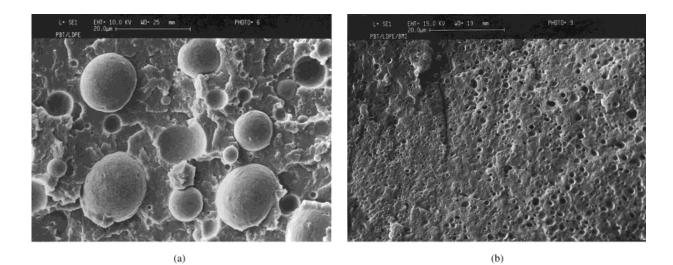
BMI can have various of reactions. Two of these are relevant to our study. (1) Nucleophilic addition to double bonds. The maleimide carbon—carbon double bond is strongly electrophilic and can react with nucleophilic reagents, such as amines, thiols, and possibly alcohol. This type of reaction have been used in polyimide synthesis and has been extensively reviewed.¹⁷ (2) Thermally induced polymerization. When BMIs are heated to above their melting point, they polymerize by an addition mechanism,¹⁸ forming a crosslinked network. Both of these reactions can take place in the melt-blending processes studied

in this work. PBT has —OH end groups, which have the possibility to react with BMI, and also the high temperature of melt mixing can induce thermal polymerization. Thus, when BMI was added to the blend melt, it is likely to polymerize rather than remain as a small molecule. The possibility of forming a PBT-BMI graft copolymer *via* nucleophilic addition of the —OH end group in PBT to the double bond of BMI should also be considered.

Because BMI is a compatibilizer for PBT/LDPE and PBT/EPDM blends, it must able to react with LDPE and EPDM. Under low temperature and low shear conditions, no reaction would be possible, because there are no functional groups available for any reaction in LDPE, and although EPDM contains some double bonds, it is very unreactive toward BMI.

However, under the melt mixing conditions, polymers are subjected to strong shear forces and high temperatures. The mechanical and thermal rupture of chemical bonds is inevitable, and formation of macroradicals is an inherent characteristic of the mixing process. The LDPE or EPDM macroradicals can easily add to the double bond of BMI, and, therefore, form LDPE-BMI or EPDM-BMI copolymers. Herein, BMI could mean the BMI monomer or its polymer, and is more likely to be the polymer because the monomer can undergo thermally induced polymerization. Because each BMI monomer has two double bonds, it is reasonable to anticipate that the BMI polymer contains many double bonds as reactive sites for further reactions. Therefore, the PBT macroradicals can react with LDPE-BMI or EPDM-BMI copolymer to form LDPE-BMI-PBT or EPDM-BMI-PBT terpolymer. It is the *in situ* formation of LDPE-BMI-PBT or EPDM-BMI-PBT terpolymer that acts as the compatibilizer.

To justify this proposed mechanism, a stabilizer (0.5 wt %) was added to the blends before the addition of BMI, and mixing conditions were kept the same as for those blends without the stabilizer. The rationale is that the stabilizer will kill all the stress and thermally induced macroradicals and, hence, stop the whole compatibilization process. Figure 2 shows transmission electron microscopy micrographs for the PBT/LDPE and PBT/EPDM blends containing both BMI and stabilizer. The particle size of the dispersed phase are the same as those of the PBT/LDPE and PBT/ EPDM blends. The presence of stabilizer has removed all the beneficial effects of BMI. This indi-



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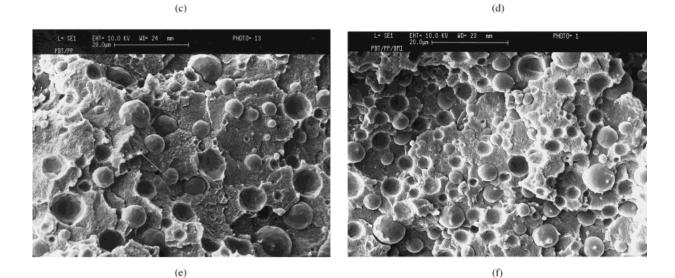


Figure 1 SEM micrographs of blends: (A) PBT/LDPE; (B) PBT/LDPE with 1.2% BMI; (C) PBT/EPDM; (D) PBT/EPDM with 1.2% BMI; (E) PBT/PP; (F) PBT/PP with 1.2% BMI; (G) PBT/PS; and (H) PBT/PS with 1.2% BMI.

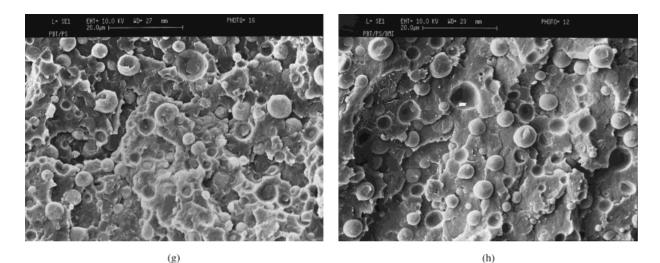


Figure 1 (Continued from the previous page)

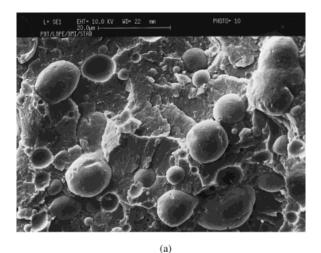
cates that free-radical reactions are definitely involved in the compatibilization process.

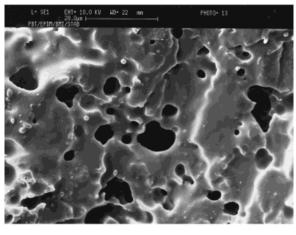
Figure 3 shows the effect of BMI content on the morphology of PBT/LDPE and PBT/EPDM blends. By increasing the BMI content from 0.3 wt % to 2.5 wt %, the particle size of the dispersed phase has only decrease a little for PBT/EPDM blend, whereas it is almost unchanged for PBT/LDPE blends. It seems that BMI content is not very important in the compatibilization process at least at the levels investigated in this study.

Effect of BMI on Rheological Properties

Figure 4 shows torque versus time date obtained during melt mixing for the parent polymers and their blends. It shows the effect of BMI on rheological properties. Figure 4(A) is for PBT; it shows the torque increase with time after the addition of BMI. At the early stage of mixing, the increase in torque is slow, but it gradually speeds up with increasing mixing time and then becomes slower again to reach a plateau value. The increase in torque is an indication of reaction taking place between BMI and PBT. It leads to an increase in molecular weight of PBT. Figure 4(A) also shows the addition of stabilizer has inhibited the reaction because no increase in torque was observed.

Figure 4(B,C) shows that the addition of BMI gives a very large and very rapid increase in torque for LDPE and EPDM. Even a BMI content as low as 0.1 wt % can lead to a 50% increase in torque, and the extent of torque enhancement increases with the amount of BMI added. The whole process of torque increase is completed





(b)

Figure 2 SEM micrographs of blends: (A) PBT/LDPE with 1.2% BMI and 0.3% stabilizer; and (B) PBT/EPDM with 1.2% BMI and 0.3% stabilizer.

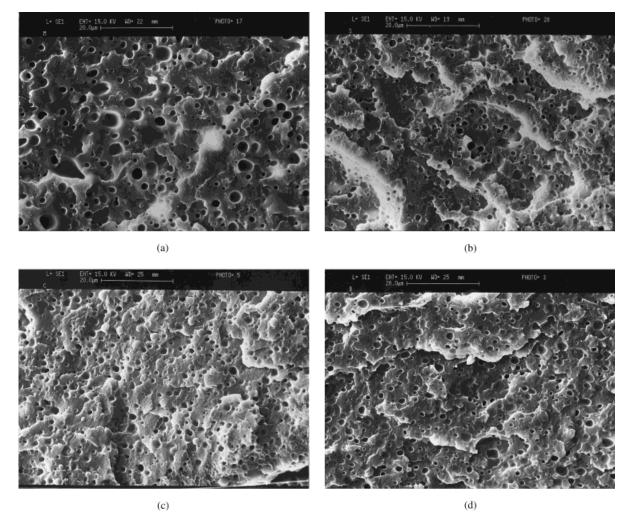


Figure 3 SEM micrographs of blends: (A) PBT/EPDM with 0.3% BMI; (B) PBT/EPDM with 2.5% BMI; (C) PBT/LDPE with 0.3% BMI; and (D) PBT/LDPE with 2.5% BMI.

within 2 min, which means the reaction between BMI and LDPE or EPDM is very fast. Then the torque decreases and gradually falls to a steady value. This decrease is the result of mechanical degradation of the polymer chains. The reactions between BMI and LDPE or EPDM are more extensive than that with PBT. This can arise from different reasons. First, PBT has a different chemical structure from LDPE and EPDM. Therefore, its stability to mechanical or thermal degradation is different, and the reactivity of the resultant macroradical is also different. Second, PBT has a lower viscosity than LDPE and EPDM. This makes it less likely to undergo mechanical degradation; therefore, a lower amount of macroradicals will be formed. As shown in Figure 4(B,C), in the presence of stabilizer, the addition of BMI does not show any effect on the viscosity of either LDPE or EPDM. When both stabilizer and BMI are present, a small reduction in torque is seen just after the addition of BMI. This is possibly because the BMI is acting as a lubricant before it is immediately mixed into the polymer. Figure 4(D,E) shows that BMI does not react with PP or PS during melt mixing. This explains why BMI fails to improve the dispersion of PP or PS in PBT [see Fig. 1(E,H)]. The reasons for the inability of BMI to react with PP or PS are not clear yet, but it is suspected that the commercial sample of PP or PS may contain stabilizer.

Figure 4(F) shows the torque versus time for a PBT/LDPE blend in the presence of 1.2 wt %BMI. After PBT has completely melted, BMI is added, and the torque is recorded. The mixing was continued for 17 min before LDPE was added. During this period, the torque increased

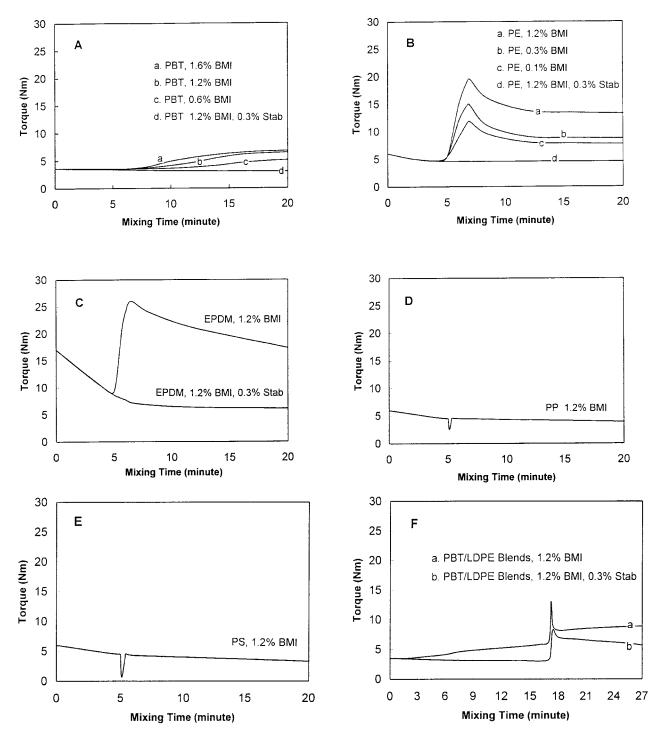
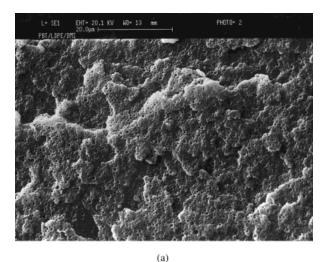


Figure 4 Torque versus mixing time recorded during melt mixing in a Haake. [BMI is added at the start in (A) and (F) and at 5 min in (B) to (E); stabilizer is added at the start.]

gradually and reached a steady level. LDPE was then added to the melt. It caused an immediate increase in torque and was then followed by a rapid decrease as the addition of LDPE into the mixing chamber changed temperature of the melt. The torque then showed a slow increase with time until the mixing was finished. When stabilizer was present in this blend, it inhibited the effect of BMI and lead to a slow decrease of torque with time.

The Effect of Mixing Sequence

It is known that the dispersed domain size in a blend increases as the viscosity of the dispersed phase increases; but, it decreases as the matrix viscosity increases, as shown by Taylor's¹ and later Wu's¹⁹ equations. As reported herein, the reaction of BMI with the matrix and the dispersed phase lead to an increase of viscosity for both phases. Therefore, it is desirable to promote a favorable increase in viscosity for the matrix and to minimize the unwanted increase in viscosity for the dispersed phase. To achieve this purpose, BMI was added to PBT melt before the addition of LDPE or EPDM to allow the reaction between BMI and PBT to occur until the viscosity of PBT was substantially increased; then, LDPE or EPDM was added and mixing was continued for a predetermined length of time. Figure 5(A) shows the morphology of a PBT/LDPE/BMI sample produced in this way. The torque versus time date for this sample are shown in Figure 4(F). The particle size of LDPE shown in Figure 5(A) is $\sim 0.5 \ \mu m$. It is much smaller than in the corresponding sample in which BMI was added after LDPE [see Fig. 1(B)]. This large reduction in LDPE particle size is due to two reasons: (1) the increase in viscosity of the matrix by the crosslinking reaction of PBT and (2) the reduction in interfacial tension by the grafting reaction between PBT and LDPE. A further experiment was designed to elucidate the contribution of viscosity increase of the PBT matrix to the reduction in particle size of the LDPE dispersed phase. The mixing sequence in this experiment was similar to that for the corresponding PBT/LDPE/BMI blend [Fig. 5(A)], the only difference is that the stabilizer was added immediately after the addition of LDPE. Because the added stabilizer can inhibit the reaction between LDPE and PBT, it can eliminate the contribution of interfacial adhesion to the particle size reduction. The morphology of this blend is shown in Figure 5(B). The LDPE particle size is larger than in Figure 5(A), but it is much smaller than in Figure 1(A). This has proved that the increase in viscosity of the matrix does help dispersion, and the BMI-induced interfacial reaction has reduced the particle size even further.



L+ SEL EHI-15.0 KU - KIP-27 - m POTD-15

(b)

Figure 5 SEM micrographs of blends: (A) PBT/LDPE with 1.2% BMI, and (B) PBT/LDPE with 1.2% BMI and 0.3% stabilizer. (LDPE is added after 17 min of melt mixing of PBT with BMI.)

CONCLUSIONS

This work has studied the compatibilization of PBT/LDPE and PBT/EPDM blends by using BMI. The particle sizes of LDPE or EPDM can be reduced for > 10 or 20 times by adding 1.2 wt % of BMI to the blends. The torque versus time date recorded during melt mixing shows that the addition of BMI to PBT, LDPE, EPDM, and their blends leads to a significant increase in viscosity of the melt, which indicates that reactions have taken place between BMI and the polymer during the melt-mixing process. It is plausible that these reactions are occurring via a stress or thermally induced free radical mechanism because the reaction can be inhibited by a stabilizer.

By considering both the mechanochemical reaction during melt mixing and the reactivity of BMI, a possible mechanism for the *in situ* compatibilization of PBT/LDPE and PBT/EPDM blends by BMI was proposed. This is that the shear force during melt mixing causes chemical bond rupture of the polymers, which form macroradicals of PBT, LDPE, or EPDM. These macroradicals react with BMI to form PBT-BMI-LDPE or PBT-BMI-EPDM terpolymers, and these *in situ* formed terpolymers act as compatibilizers to reduce the particle size of the dispersed phase. Because all the evidence presented in this article is indirect, the detailed mechanism needs further study.

It has also been shown that the blending sequence of the components affects the morphology of the blends. An early addition of BMI and a later addition of LDPE can give a favorable increase in viscosity of PBT and avoid the unfavorable increase in viscosity of LDPE, which improves the dispersion of LDPE in the PBT matrix.

This work shows good prospect for application of mechanochemical reactions in the field of reactive blending of polymers.

REFERENCES

- Taylor, G. I. Proc R Soc Lond, Ser A 1932, 138, 41; 1934, 146, 501; 1954, 226, 34.
- 2. Wu, S. Polymer 1987, 27, 335.
- Fayt, R.; Jerome, R.; Teyssie, Ph. J Polym Sci, Polym Lett Ed 1981, 19, 79.

- Fayt, R.; Jerome, R.; Teyssie, Ph. J Polym Sci, Polym Phys Ed 1982, 20, 2209.
- 5. Fayt, R.; Jerome, R.; Teyssie, Ph. J Polym Sci, Polym Phys Ed 1989, 27, 775.
- Cimmino, S.; D'Orazio, L.; Greco, R.; Maglio, G.; Malinconico, M.; Mancarella, C.; Martuscelli, E.; Palumbo, R.; Ragosta, G. Polym Eng Sci 1984, 24, 48.
- Tang, T.; Lei, Z. L.; Huang, B. T. Polymer 1996, 37, 3219.
- Borggreve, R. J. M.; Gaymans, R. J.; Luttmer, A. R. Makromol Chem Macromol Symp 1988, 16, 195.
- Borggreve, R. J. M.; Gaymans, R. J. Polymer 1989, 30, 63.
- Berk Tan, N. C.; Tai, S. K.; Briber, R. M. Polymer 1996, 37, 3509.
- 11. Park, C. D.; Jo, W. H. Polymer 1996, 37, 3055.
- 12. Sneller, J. A. Mod Plast Int 1985, 15(3), 42.
- Lee, P. C.; Kuo, W. F.; Chang, F. C. Polymer 1994, 35, 5641.
- Casale, A.; Porter, R. S. Polymer Stress Reactions, Vols. 1 & 2; Academic Press: New York, 1978.
- Porter, R. S.; Casale, A. in Encyclopedia of Polymer Science and Technology, H. Mark, N. M. Bikales, C. G. Overberger, G. Menges, Eds.; Wiley: New York, 1988, Vol. 9, 2nd ed.; pp 467–485.
- Greco, R.; Musto, P.; Ragosta, G.; Scarinzi, G. Makromol Chem, Rapid Commun 1988, 9, 129.
- Stenzenberg, H. D.; Herzog, M.; Römer, W.; Scheiblich, R.; Reeves, N. J. Br Polym J 1993, 15, 2.
- Stenzenberg, H. D. J Appl Polym Sci, Appl Polym Symp 1977, 31, 91.
- 19. Wu, S. Polym Eng Sci 1985, 26, 1855.