Polymer 44 (2003) 2423–2432

polymer

www.elsevier.com/locate/polymer

Reactive compatibilizer precursors for LDPE/PA6 blends. III: ethylene–glycidylmethacrylate copolymer

Valeria Chiono[a], Sara Filippi[a], Hristo Yordanov[b], Lilyia Minkova[b], Pierluigi Magagnini[a,*]

[a]*Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Università degli Studi di Pisa, via Diotisalvi 2, 56126 Pisa, Italy*
[b]*Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bontchev str., 1113 Sofia, Bulgaria*

Received 7 October 2002; received in revised form 15 January 2003; accepted 3 February 2003

Abstract

The effectiveness of a commercial ethylene–glycidylmethacrylate copolymer (Lotader GMA AX 8840) as a compatibilizer precursor (CP) for blends of low density polyethylene (LDPE) with polyamide-6 (PA) has been evaluated by an investigation of the thermal properties and the morphology of binary (LDPE/CP and PA/CP) and ternary (LDPE/PA/CP) blends, as well as by solvent fractionation experiments. It has been demonstrated that the epoxy groups of the CP react quite easily, during melt blending, with both the amine and the carboxyl end groups of PA to give CP-*g*-PA copolymers, which, depending on the relative amounts of PA and CP, may be partially cross-linked. The composition of the graft copolymers has been approximately determined by gravimetric and calorimetric measurements. The compatibilizing efficiency of the CP employed in this work has been found to be comparable to that of the ethylene–acrylic acid copolymers, and lower than that of a maleic anhydride-functionalized polyethylene, which had been used in previous works.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: LDPE/PA blends; Ethylene–glycidylmethacrylate compatibilizer precursor; Morphology

---

1. Introduction

Blends of polyethylene (PE) with polyamide-6 (PA) must be appropriately compatibilized if materials with attractive properties are sought for. Many different compatibilizers that proved useful for PE/PA blends have been described in the scientific and patent literature [1,2]. It has been shown, for example, that polyolefins functionalized with maleic anhydride or acrylic acid behave as efficient compatibilizer precursors (CPs) for these blends, as they react with PA, during blending, to produce CP-*g*-PA copolymers which act as the true compatibilizers [3–8]. Preformed copolymers of ethylene with vinyl acetate [5] or with esters of the acrylic (or methacrylic) [9,10] and succinic [11] acids have also been used for compatibilization. Other compatibilizing agents that have been found to be efficient are the copolymers of ethylene with acrylic or methacrylic acid neutralized with sodium or zinc (ionomers) [12–14]. Functionalization of PE with oxazoline groups also yielded good CPs, capable of reacting rapidly with the amine and/or the carboxyl end groups of PA [15].

In previous works, the reactive compatibilization of blends of low density polyethylene (LDPE) with PA, carried out using two types of CPs, namely, ethylene–acrylic acid copolymers (EAA) [16] and maleic anhydride grafted polyethylenes (PE-*g*-MA) [17], has been investigated. The relative effectiveness of the two types of CPs has been studied comparing their reactivity toward PA and their emulsification ability. It was shown that the efficiency of these CPs depends, not only on the reactivity, the concentration and the distribution along the polyolefin chain of the functional groups, but also on the CP melt viscosity and its miscibility with the polyethylene phase [16,17].

In the present work we have investigated the behavior of another CP, consisting of an ethylene–glycidylmethacrylate copolymer (EGMA), and have compared its effectiveness with that of the two CPs studied earlier [16,17]. In order to obtain readily comparable results, the same LDPE/PA blends and the same blending and characterization conditions have been used throughout. Previous works by others had shown that GMA functionalized polyolefins

---

* Corresponding author. Tel.: +39-050-511222; fax: +39-050-511266.
E-mail address: magagnini@ingunipi.it (P. Magagnini).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00134-4

behave as effective CPs, e.g. for blends of poly(ethylene terephthalate) (PET) with high density polyethylene (HDPE) or with ethylene-*co*-propylene rubber (EPR) [18–21]. Also, attempts to compatibilize blends of poly(butylene terephthalate) (PBT) with polyolefins have been made using random or graft copolymers of GMA [22–25]. Rubbers functionalized with GMA have been employed as toughening agents for various polyesters [26,27]. Styrene–GMA copolymers were also used to compatibilize polystyrene/polyamide blends [28]. The effect of the chemical interactions taking place between polyamide-10,10 and a PP-*g*-GMA copolymer on the morphology and the properties of their blends was studied by Zhang et al. [29]. The EGMA copolymer used in this work had already been employed by Koulouri et al. [30] in binary blends with different polyamides. These authors found that the most efficient grafting of polyamide chains onto the EGMA backbone occurred with the EGMA/polyamide-11 blends, and explained the observed reactive compatibilization effects as being due to the reaction of the amine end groups of the polyamides with the epoxide rings of EGMA. However, previous studies had demonstrated that both amines [31–35] and carboxylic acids [33,36] are capable of reacting with epoxide groups, and this was recently confirmed by Kudva et al. in a study of the compatibilization of PA/ABS blends with GMA-methyl methacrylate copolymers [37]. Through model rheometry experiments, these authors proved that cross-linking reactions take place between copolymers containing GMA moieties and low molar mass diamines or diacids and pointed out that similar reactions can also occur between the GMA copolymers and PA. They postulated that the cause of the poor dispersion of ABS droplets they observed was the capability of the PA chains to react with the epoxide rings of GMA through both the amine and the acid end groups, and to form complex loops and bridge structures which hinder the dispersion or causes the agglomeration of the ABS particles. Finally, Tedesco et al. [38] studied the morphology and the thermal and mechanical properties of 70/30 blends of polypropylene (PP) and PA, compatibilized with 7 wt% of a PP-*g*-GMA copolymer containing 0.32 mol% of functional groups, and found that the compatibilizing efficiency of this copolymer was rather poor.

In order to shed more light on the chemical interactions taking place during melt blending between PA and EGMA, a fairly detailed study of the binary blends was carried out in this work, before dealing with the thermal and morphological investigation of the ternary LDPE/PA/EGMA blends.

2. Experimental

2.1. Materials

Two grades of LDPE, kindly provided by Polimeri Europa, were used: Riblene FF20 with a melt flow index (MFI) equal to 0.8 g/10 min, referred to herein as LD08, and Riblene FC30 with MFI = 0.3 g/10 min, referred to as LD03. Polyamide-6 (PA) was a commercial sample, kindly supplied by Snia Tecnopolimeri, with a relative viscosity in sulfuric acid (95.7%) of 3.66 and contents of amine and carboxyl end groups of 34 and 35 mequiv./Kg, respectively. The CP was an ethylene–glycidylmethacrylate copolymer (Lotader GMA AX8840) provided by Elf-Atochem, referred to herein as EGMA. It contains 8 wt% GMA and has MFI equal to 5.0 g/10 min. Before use, all the polymers were accurately dried under vacuum for 12 h at 70 °C (for the PE and EGMA) or 120 °C (for PA).

2.2. Blends preparation

For the preparation of the binary (PE/CP and PA/CP) and ternary (PE/PA/CP) blends, the selected amounts of the components, dried as described above, were dry-blended and charged into the 50 ml static mixer of a Brabender Plasticorder, preheated to 235 °C. The rotor speed was held about 1 min at 30 rpm and was then increased to 60 rpm. Blending was continued under nitrogen for about 4 min (up to constant torque).

2.3. Solvent etching and fractionation

85% formic acid, xylene and phenol (Aldrich) were used for the fractionation and etching experiments. The Molau test [39,40] was performed for the PA/EGMA binary blends by stirring about 2 g of finely powdered material in 50 ml of 85% formic acid and storing the test tubes for 24 h. The formation of a stable suspension or of a turbid colloidal solution was taken as an indication of the presence of a PA-*g*-CP copolymer acting as a surfactant. Quantitative solvent fractionation experiments were also carried out on the binary blends using formic acid and hot xylene as selective solvents. A blend sample was treated first with formic acid and the insoluble fraction was separated by centrifugation of the suspensions, washed with the pure solvent, dried and weighed. The remaining solution, which was sometimes opalescent or even turbid, was poured into excess methanol and the precipitate was washed with pure methanol, dried and weighed. The insoluble fraction was extracted further by repeated treatments with hot xylene to obtain a xylene soluble and a xylene insoluble fraction. All fractions were analyzed by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), FTIR spectroscopy, etc. Other particular solubility experiments were carried out in a few instances using phenol/xylene mixtures, as described in the Results section.

2.4. Blends characterizations

Scanning electron microscopic analysis (SEM) was made with a JEOL JSM-5600 apparatus on polymer specimens fractured under liquid nitrogen and coated with gold. The size and the size distribution of the dispersed phase droplets were determined on at least two micrographs taken on solvent etched fracture surfaces of each sample with an automatic image software, measuring the diameter of at least 500 droplet marks. The number average diameter (d_n) was calculated from the relationship $d_n = \sum(n_i d_i)/\sum n_i$, where n_i is the number and d_i is the diameter of the ith droplet.

Differential scanning calorimetry (DSC) measurements were carried out under nitrogen, on samples of 5–8 mg, using a Pyris Perkin Elmer apparatus calibrated with indium and tin standards. The pure polymers were pretreated in the Brabender mixer under the same conditions used for blending. The scanning rate was of 10 K/min. The first heating scan was carried out from 20 to 250 °C and the sample was held at this temperature for 3 min, to cancel the thermal history effects, before starting the cooling and the second heating sweeps, which were used for figures and tables. The temperature ranges used for measuring the ΔH values were normally as follows: 70–110 °C (cooling) and 75–125 °C (heating) for the PE and EGMA phases and 170–195 °C (cooling) and 185–235 °C (heating) for the PA phase. The values of ΔH were usually normalized to the amount of the phase under consideration in order to get information on its degree of crystallinity. ΔH values normalized to the overall amount of the sample were used, e.g. in Table 2, whenever the exact concentration of the relevant component was unknown and was just approximately calculated from the ΔH values.

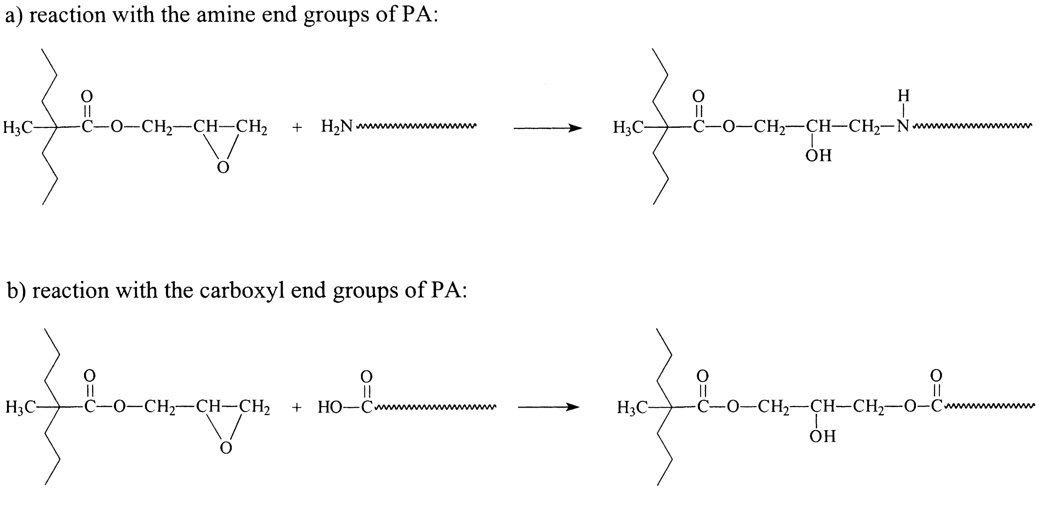
For the isothermal crystallization experiments, samples of uncompatibilized and compatibilized blends were heated to 190 °C (for a study of the LDPE phase crystallization), or to 250 °C (for the PA phase crystallization) in order to destroy the LDPE or PA crystal nuclei, kept at this temperatures for 5 min, and cooled to the selected crystallization temperature T_c with a rate of 320 K/min. T_c was in the range 102–106 °C for the crystallization of the LDPE component, and in the range 195–199 °C for the crystallization of the PA phase. The heat evolved during isothermal crystallization was recorded, and the fraction X_t of the polymer crystallized at time t was evaluated as the ratio of the area under the curve at time t to that of the whole exotherm. The starting time of crystallization was taken as that at which thermal equilibrium was reached at T_c. The area of the exotherm was measured by back extrapolation of the baseline after complete crystallization.

3. Results and discussion

3.1. Binary blends

The possible reactions between EGMA and PA, which can lead to the formation of PA-*g*-EGMA copolymers are indicated in the scheme below (Scheme 1).

Kudva et al. [37] have studied the kinetics of the reactions of epoxide rings with amine and with acid groups, under the melt processing conditions, by recording the torque applied to the Brabender mixer while incorporating into EGMA low molar mass compounds modeling the end groups of PA. They showed that incorporation of 2% of monoacid or monoamine had negligible effect on the melt viscosity of EGMA, whereas very rapid increases in torque were recorded after addition of a diacid or a diamine. They concluded that both reactions shown in the scheme take place easily and rapidly in the blending conditions. On the contrary, the hypothetical reactions of GMA with the hydroxyl functionalities generated by amine-epoxide and acid-epoxide ring-opening reactions were found not to play a significant role, and those with the secondary amines produced by the amine-epoxide reaction to be quite slow relative to the time scale of reactive processing. In conclusion, with respect to the CPs based on EAA and PE-*g*-MA copolymers, which can only form amide bridges with the PA chains, the EGMA copolymer employed in this work can react with both end groups of PA and, therefore, it should also be capable of yielding cross-linked products if



Scheme 1.

Table 1
Torque measured while blending PA with EGMA in the Brabender at 235 °C and 60 rpm

Blend composition (EGMA/PA wt/wt)	Torque (N m)
0/100	12.8
10/90	16.3
20/80	19.7
50/50	9.8
100/0	6.1

more than two GMA units per chain react. Although the molecular weight of the EGMA sample used in this work is unknown, it can be argued from the MFI and the mass concentration of GMA that the number of functional groups per macromolecule is certainly much higher than 2. Thus, to avoid cross-linking, either a very low concentration or a strong excess of EGMA with respect to PA should be employed. Simple calculations based on the concentration of reactive units in the chains of PA (69 mmol/Kg) and EGMA (563 mmol/Kg) show that stoicheiometric equivalence is approximately obtained when the two polymers are blended in the 90/10 wt/wt ratio.

Qualitative confirmation that chemical interactions do actually occur between PA and EGMA, in the blending conditions, was obtained by measuring the torque applied for the preparation of the binary 90/10, 80/20 and 50/50 w/w PA/EGMA blends, at 235 °C and 60 rpm (cf. Table 1). In fact, the torque of the blends having PA as the continuous phase increases appreciably as the EGMA concentration increases, despite the lower viscosity of the latter component, whereas it becomes close to that calculated with the additive rule for the 50/50 w/w ratio, i.e. after phase inversion has taken place.

The 90/10 and 80/20 PA/EGMA blends were treated with formic acid as described in the experimental section and yielded fairly stable turbid suspensions. No such treatment could be applied to the 50/50 blend because it had EGMA as the matrix. A control experiment was carried out with a 80/20 PA/LD08 blend. As expected, this gave a clear PA solution and a supernatant layer of insoluble LD08 particles. These results confirm that chemical reactions between the epoxy groups of EGMA and PA do in fact take place during blending.

The formic acid suspension obtained from the 90/10 PA/EGMA blend proved very stable and it was impossible to separate an insoluble fraction from it. This demonstrates that, in this blend, most of the EGMA macromolecules are grafted with PA sequences and become either soluble in formic acid or capable to form colloidal particles that cannot settle even after prolonged centrifugation.

The behavior of the turbid formic acid suspension of the 80/20 blend was quite different. In this case, in fact, centrifugation allowed the separation of a formic acid insoluble fraction (R^1_{insol}) from an opalescent solution; the solution was poured into methanol to yield the 'soluble'

Table 2
Thermal properties of PA, EGMA and fractions of the 20/80 EGMA/PA blend and yields and calculated compositions of the fractions

Samples and fractions	Yield (wt%)	EGMA phase				PA phase				Composition EGMA/PA (wt/wt)
		T_c (°C)	ΔH_c [a] (J/g)	T_m (°C)	ΔH_m [a] (J/g)	T_c (°C)	ΔH_c [a] (J/g)	T_m (°C)	ΔH_m [a] (J/g)	EGMA
		91.6	78.6	105.2	76.9	–	–	–	–	100/0
PA		–	–	–	–	187.6	69.8	219.4	67.7	0/100
EGMA/PA		93.3	13.0	103.7	11.7	188.3	46.8	219.4	45.6	20/80
R^1_{sol}	76.0	87.1	3.3	100.3	2.5	187.8	68.6	218.1	65.6	3/97
R^1_{insol}	24.0	88.8	35.9	102.8	41.4	181.0	17.1	212.6	17.6	69/31
R^2_{insol}	17.9	88.3	29.7	100.1	32.2	180.3	23.0	211.2	25.9	55/45
R^2_{sol}	6.1	95.2	78.2	106.6	79.0	–	–	–	–	100/0

[a] Values normalized to the overal amount of the sample.

fraction R^1_{sol}. As described in Section 2, R^1_{insol} was repeatedly washed with pure formic acid, with no weight loss, and was then treated with boiling xylene to give an insoluble residue (R^2_{insol}) and a clear solution from which the xylene soluble fraction R^2_{sol} was recovered by precipitation into excess methanol. The yields of the four fractions obtained from the 80/20 PA/EGMA blend are given in Table 2. Interestingly, the R^1_{insol} fraction was recovered with a yield of 24%, which is higher than the overall content of EGMA in the starting blend. Considering that some of the EGMA was also lost in the opalescent solution from which the soluble fraction R^1_{sol} was obtained, this result demonstrates that R^1_{insol} must contain an appreciable amount of PA, which can only be present as segments grafted onto the EGMA chains. Similar results were obtained from a study of the 80/20 blends of PA with maleic anhydride functionalized polyethylenes [17] and were interpreted considering that the PA-*g*-CP copolymers produced during blending are sufficiently rich of polyethylene segments to be predominantly insoluble in formic acid. On the contrary, when the 80/20 blends of PA with EAA copolymers were considered [16], it was found that the formic acid insoluble fraction was considerably less than expected (15% of the blend, versus an EAA initial content of 20%), thus showing that the PA-*g*-CP copolymers were in that case rich enough of PA chains to remain, at least in part, in the soluble fraction.

That the insoluble fraction R^1_{insol} does not consist simply of EGMA, but contains a graft copolymer, is demonstrated by the biphasic morphology of this material that is clearly seen in the SEM photomicrograph of the fracture surface of this material shown in Fig. 1a. In fact, the presence of a dispersed phase consisting of predominantly spherical droplets imbedded in a matrix, is clearly argued from the micrograph. Extraction with hot xylene dissolves most of the EGMA matrix and yields the R^2_{insol} residue whose morphology is shown in Fig. 1b.

The thermal data recorded by DSC for the pure polymers, for the 80/20 PA/EGMA blend and for its fractions are collected in Table 2, and the DSC cooling and second heating traces are shown in Fig. 2. All these data demonstrate that the thermal characteristics of the two soluble fractions R^1_{sol} and R^2_{sol} are very close to those of the pure blend components, although a first order transition of very low intensity associated with an EGMA phase was also visible in the DSC trace of R^1_{sol}. On the contrary, both PA and EGMA phases could be clearly detected by DSC in the insoluble fractions, thus confirming the previous conclusions concerning the presence of a PA-*g*-EGMA copolymer in the blend. Moreover, simple calculations using the ΔH_c and ΔH_m data given in Table 2 for the pure polymers and the PA/EGMA blend show that the degree of crystallinity of both components is reduced as a result of

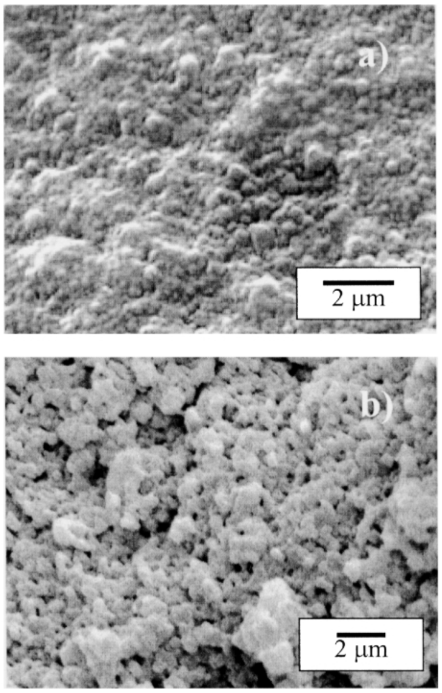


Fig. 1. SEM micrographs of the R^1_{insol} (a) and R^2_{insol} (b) fractions of the 80/20 PA/EGMA blend.

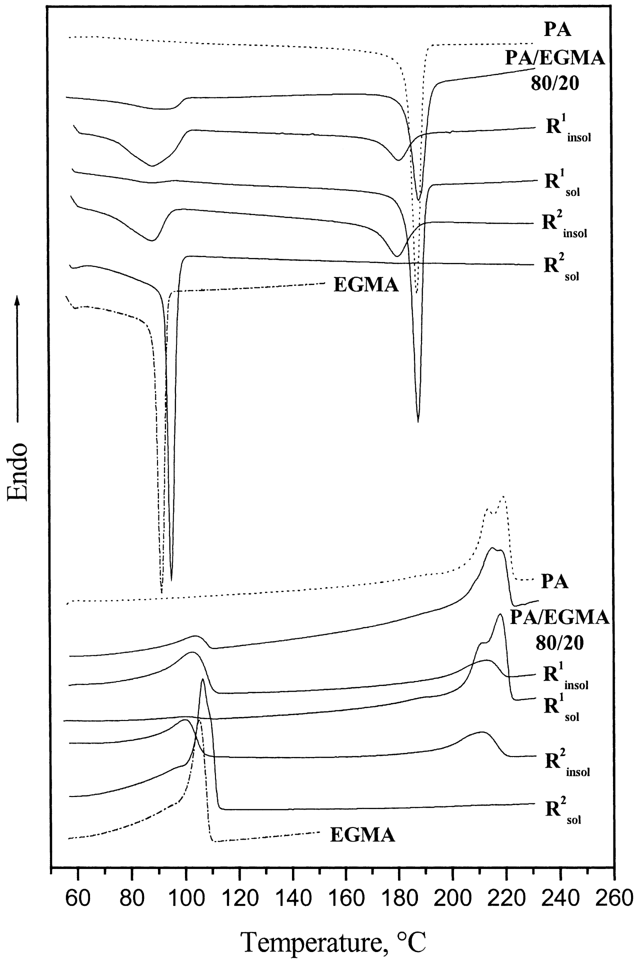


Fig. 2. DSC traces of the 80/20 PA/EGMA blend, of its components, and of its solvent separated fractions.

blending. It may be concluded, therefore, that unreacted PA and EGMA are mostly found in the R^1_{sol} and R^2_{sol} fractions, respectively, whereas the PA-*g*-EGMA copolymer is the main constituent of the R^2_{insol} fraction. Thus, in order to calculate the composition of the different materials obtained by solvent fractionation of the 80/20 PA/EGMA blend, use was made of the values of their yields (2nd column of Table 2) and of the crystallization/melting enthalpies of their two phases, compared with those of the pure components (for the R^1_{sol} and R^2_{sol} fractions) and of the PA/EGMA blend (for the R^1_{insol} and R^2_{insol} fractions). A detailed discussion of the calculation procedure was made in the previous paper of this series [17]. The estimated compositions are given in the last column of Table 2.

It can be seen that the PA-*g*-EGMA copolymer that is formed when blending PA with EGMA in the 80/20 wt ratio is found in the R^1_{sol} and R^2_{insol} fractions, the former representing about 76% and the second 18% of the whole blend. From the EGMA content of these two fractions (3 and 55%, respectively) it can be calculated that approximately two thirds of the EGMA contained in the blend was used up in the grafting reaction. The expected high reactivity of this epoxy CP is therefore confirmed. The MA grafted polyethylenes employed in the previous work [17] proved also very reactive, as 15–28% of the relevant PA/CP blends also consisted of PA-*g*-CP copolymers. However, in these copolymers the content of CP chains was lower (13–37%). This was explained considering that, at least for some of the CPs, the succinic anhydride functional groups were not statistically distributed along the polyethylene backbones and that some non-functionalized material was probably present.

The above evidences demonstrate that PA-*g*-EGMA copolymers are actually produced by the reactions of the epoxide groups of the CP with the acid and amine end groups of PA. However, they provide no information on the structure of these copolymers and, in particular, on whether they are cross-linked. To shed more light on this point, we tried to find a solvent in which a non cross-linked PA-*g*-EGMA copolymer could expectedly be soluble. A mixture composed of 35 wt% phenol and 65 wt% xilene proved suitable: in fact, a dry blend of PA and EGMA pellets dissolved rapidly and completely in this mixed solvent, under gentle stirring and upon heating to about 120 °C. The solubility of the binary PA/EGMA blends or that of their R^2_{insol} residues in this solvent mixture was then evaluated. The 90/10 PA/EGMA blend was found to be completely soluble, though it gave a weakly opalescent solution. On the contrary, the R^2_{insol} fraction recovered from the 80/20 PA/EGMA blend dissolved only partially: a gel-like residue was recovered by filtration, washed with fresh solvent and dried. This material, which was considered to be a cross-linked PA-*g*-EGMA copolymer, amounted to about two thirds of the R^2_{insol} sample, or about 12% of the initial 80/20 PA/EGMA blend (cf. Table 2). The 50/50 PA/EGMA blend, which could not be fractionated by the usual sequence of treatments in formic acid and xylene because it had PA as the dispersed phase, was also treated with the mixed solvents in order to dissolve all unreacted PA and EGMA, as well as any eventual non cross-linked PA-*g*-EGMA copolymer. The gel-like residue was isolated and weighed and was found to be about 16% of the initial blend. These experiments provide direct demonstration of the possibility that cross-linked graft copolymers can actually result from the concomitant occurrence of both the amine-epoxide and acid-epoxide reactions under the processing conditions used for the blends preparation. However, they also suggest that cross-linking may probably be of little importance when EGMA is used as a CP additive with a concentration of about 2 phr, as it was done in the second part of this work.

Finally, a DSC and SEM investigation of the LDPE/EGMA binary blends was also carried out and confirmed the results found previously for other blends of LDPE with CPs consisting of functionalized HDPE samples [16,17]. In fact, the two polymers are immiscible, though being highly compatible. This situation is most favorable for the compatibilization of LDPE/PA blends, because the CP tends to migrate to the interface rather than being dissolved within the LDPE phase. In a previous work [17], the LDPE-*g*-MA copolymers were found to be miscible with LDPE and their poor CP effectiveness was attributed to scarce availability at the LDPE/PA interface where grafting is expected to occur.

3.2. Ternary Blends

The blends of LD08 and LD03 with PA were prepared in the whole composition range, both without and with 2 phr EGMA. For the 75/25 LD08/PA blend, the amount of added CP was varied between 0 and 8 phr. The ternary blends discussed in the present paper are indicated in Table 3. The thermal properties of the blends, also collected in Table 3, demonstrate that the addition of 2 phr EGMA has negligible effect on the temperatures of melting and crystallization of both blends components, as well as on the melting and crystallization enthalpies of the LDPE phase. The enthalpies associated with fusion and crystallization of the PA phase, on the contrary, are somewhat reduced when EGMA is present, thus confirming that there are fairly strong interactions between the CP and PA. These results are very similar to those found for the ternary blends compatibilized with the EAA copolymers [16] or with the MA-functionalized polyethylenes [17]. However, no indication of a fractionated crystallization of the PA phase, similar to that found for the blends with a PA concentration of 10 or 25 wt% compatibilized with the above CPs [16,17], was observed in the present investigation. This seems to indicate that the reduction of the PA droplet size caused by EGMA is smaller than that found with the other CPs, or, alternatively, that this compatibilizer may act itself as a heterogeneous nucleating agent for PA.

The isothermal crystallization of the LDPE/PA blends,

Table 3
Composition and thermal properties of the ternary LD08/PA/CP and LD03/PA/CP blends

Blend	LDPE phase				PA phase			
	T_c (°C)	ΔH_c[a] (J/g)	T_m (°C)	ΔH_m[a] (J/g)	T_c (°C)	ΔH_c[a] (J/g)	T_m (°C)	ΔH_m[a] (J/g)
LD08/PA/EGMA								
100/0/0	96.6	82.3	110.9	84.0	–	–	–	–
90/10/0	97.9	76.5	111.1	92.8	185.8	39.3	219.3	47.7
90/10/2	97.6	81.9	110.0	93.2	187.8	46.4	218.6	43.5
75/25/0	98.1	78.6	111.7	97.4	188.0	66.0	220.3	67.7
75/25/1	97.2	77.3	109.7	89.9	187.1	43.1	217.9	48.1
75/25/2	97.8	81.5	110.6	95.7	187.7	46.4	219.1	43.5
75/25/3	98.0	79.8	110.0	96.1	186.7	51.0	218.4	52.2
75/25/5	97.0	78.6	110.5	89.5	186.3	53.9	218.9	46.8
75/25/7	97.0	78.6	109.9	87.8	186.3	53.9	218.4	53.1
60/40/0	98.6	79.4	110.3	94.0	189.2	72.3	219.3	67.7
60/40/2	98.3	76.9	110.2	86.1	189.0	58.1	219.1	53.1
40/60/0	97.9	77.7	110.4	84.0	188.8	68.1	219.3	64.8
40/60/2	98.2	77.3	109.7	84.4	189.9	59.4	214.1	55.6
25/75/0	98.2	77.7	109.7	85.3	188.8	69.8	218.9	68.1
25/75/2	98.3	78.2	109.4	75.2	189.6	62.7	215.5	60.2
10/90/0	98.7	66.9	108.6	70.2	189.0	66.5	218.8	66.9
10/90/2	98.7	73.2	108.5	59.8	189.3	66.0	219.1	60.2
0/100/0	–	–	–	–	187.6	69.8	219.4	67.7
LD03/PA/EGMA								
100/0/0	97.6	80.3	110.4	87.4	–	–	–	–
90/10/0	98.6	83.6	110.1	99.9	188.6	23.0	218.6	50.2
90/10/2	97.8	81.5	110.0	98.2	187.3	37.2	218.0	38.5
75/25/0	98.6	82.8	109.7	97.4	188.5	52.2	218.8	54.3
75/25/2	97.5	78.6	111.0	92.0	189.1	51.8	214.4	54.3
60/40/0	98.0	80.3	111.1	92.0	188.6	64.8	219.8	64.8
60/40/2	98.0	85.3	110.0	97.4	189.6	48.9	218.9	51.4
40/60/0	98.2	80.3	110.4	84.0	188.8	70.6	218.0	66.9
40/60/2	98.3	77.3	109.7	84.8	190.3	66.9	214.6	64.8
25/75/0	98.2	77.7	109.7	85.3	188.8	69.8	218.9	68.1
25/75/2	98.2	76.5	108.7	70.6	189.7	66.9	215.3	59.9
10/90/0	98.8	65.2	108.2	67.7	189.2	66.0	218.7	63.9
10/90/2	98.3	74.0	107.4	69.4	189.9	59.4	214.4	64.0
0/100/0	–	–	–	–	187.6	69.8	219.4	67.7

[a] Values normalized to the amount of the relevant phase.

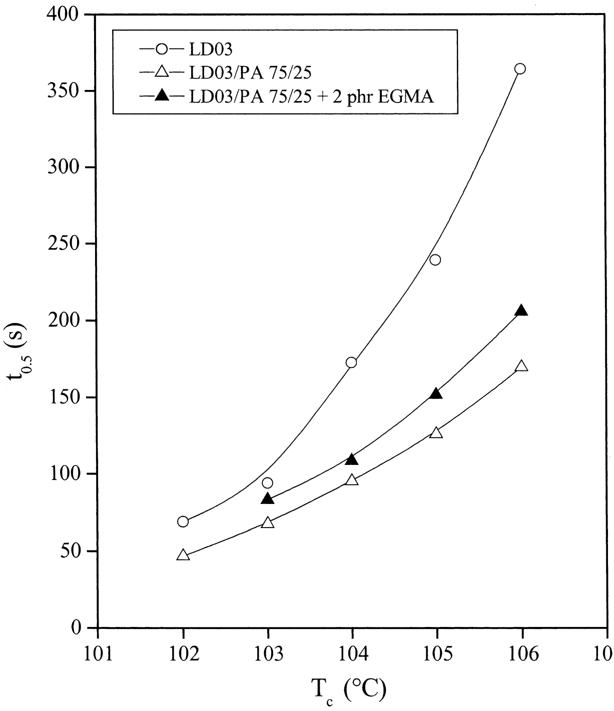


Fig. 3. Half crystallization times of the LD03 phase as a function of the isothermal crystallization temperature for neat LD03 and its 75/25 blends with PA, without and with 2 phr EGMA.

without and with EGMA, as well as of the pure components, were studied in two ranges of temperatures: $T_c = 102-106$ °C, for the crystallization of the LDPE phase, and $T_c = 195-199$ °C, for the crystallization of the PA phase. The half-crystallization times ($t_{0.5}$) were determined and taken as an inverse measure of the crystallization rates. The results show that the LDPE crystallization rate increases when this polymer is blended with PA. This means that the crystalline PA phase acts as a nucleating agent for the LDPE crystallization, and the observation that the effect is practically independent of the PA concentration suggests that the number of heterogeneous nuclei remains almost constant as the increase of PA concentration is paralleled by that of the particles size. The addition of 2 phr EGMA into the blends leads to a decrease of the overall crystallization rate, although the latter remains still higher than that of neat LDPE. These effects are exemplified by the plots in Fig. 3, showing the temperature dependence of the half-crystallization time $t_{0.5}$ for pure LD03 and the LD03 phase of the 75/25 LD03/PA blends without and with 2 phr EGMA. The crystallization rate of LD03, both neat and blended, was slightly lower than that of LD08, probably due to the higher molar mass of the former polymer. Except for this, the behavior of all the investigated blends was very similar to that illustrated in Fig. 3. The decrease of the overall crystallization rate of the LDPE phase resulting from the addition of EGMA into the blends suggests that the interactions between the compatibilizer and LDPE disturb the crystallization of the latter. This was also observed in a previous study of the isothermal crystallization of binary 80/20 LDPE/EGMA blends [41].

The results of the isothermal calorimetry experiments reveal that the molten LDPE phase also acts as a nucleating agent for the PA crystallization. The effect is illustrated in Fig. 4, where the half times of crystallization $t_{0.5}$ of pure PA and of the PA phase of the 75/25 LD08/PA blends without and with 2 phr EGMA are plotted as a function of Tc. The addition of EGMA leads to an increase of the half-crystallization times, but these remain still smaller than that recorded for neat PA.

Treatment of the blends with selective solvents allowed the identification of the composition corresponding to phase inversion. The blends of PA with LD08, both with and without added EGMA, were found to undergo phase inversion in the composition range between 60 and 75% PA. For the blends with LD03, phase inversion was shown

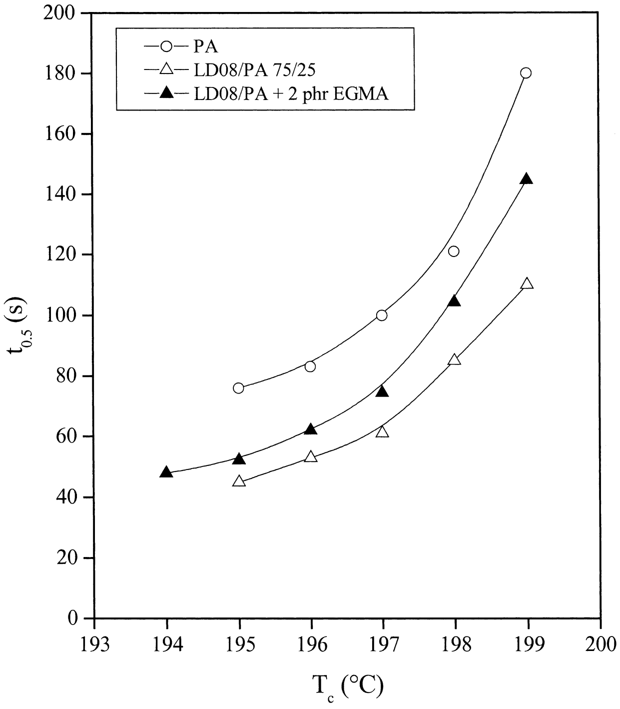


Fig. 4. Half crystallization times of the PA phase as a function of the isothermal crystallization temperature for neat PA and its 25/75 blends with LD08, without and with 2 phr EGMA.

to occur in the 40–60% PA range, in the absence of compatibilizer, and in the 60–75% range, when the CP was present. This behavior can be tentatively rationalized considering the viscosity ratio of the two phases in each blend and the viscosity increase of the PA phase caused by the EGMA addition (cf. Table 1).

The morphology of the ternary blends was studied by SEM. Examples of the SEM micrographs are shown in Fig. 5 for the 75/25 LDPE/PA blends, with and without EGMA, and in Fig. 6 for the corresponding blends with 40/60 composition. A quantitative evaluation of the size reduction of the minor phase particles was sometimes impossible because the latter had irregular geometry in some of the uncompatibilized blends, such as the 75/25, 60/40 and 40/60 LD03/PA and the 40/60 LD08/PA (cf. Figs. 5 and 6). Nevertheless, the morphological characterization clearly demonstrated that the addition of 2 phr EGMA into the LDPE/PA blends causes a strong improvement of the minor phase dispersion. As already found for the other CPs employed previously [16,17], the effect was particularly evident for the blends containing the higher viscosity LDPE sample (LD03).

The dependence of droplet size on the EGMA concentration was studied for the 75/25 LD08/PA blends. The emulsification curve is presented in Fig. 7, together with those obtained in previous works for the same blend composition, by the use of CPs consisting of EAA copolymers [16] and MA-functionalized polyethylenes [17]. We may observe that the strongest reduction of droplet size takes place, for all the CPs except LD08-*g*-MA, in the CP content interval between 0 and 1–3 phr, the upper limit being probably influenced by the concentration of the functional groups in the CP chains (1.7 mol% for EGMA, 2.5 mol% for EAA, and 0.3 mol% for l-HDPE-*g*-MA). Notice that the low effectiveness of LD08-*g*-MA, whose functional groups concentration (0.876 mol%) was three times that of l-HDPE-*g*-MA, was ascribed to its miscibility with the LD08 matrix, and to its slow migration to the interface where reaction with the PA is expected to take place. The curves in Fig. 7 show that the behavior of the CP studied in this work is similar to that of the EAA copolymers. The effectiveness of both these CPs, however, appears to be considerably lower than that of l-HDPE-*g*-MA. In fact, the latter causes a much stronger reduction of the PA droplets size, though having a smaller concentration of functional groups. Based on the information on the reactivity of the carboxyl, the anhydride and the epoxide groups provided by the investigation of the binary CP/PA blends, we would expect EGMA to be at least as effective as the PE-*g*-MA copolymers, and much more efficient than the EAA copolymers. The experimental results demonstrate that this is not so. Although the effectiveness of the EGMA copolymer studied in this work was considerably higher than that of the PP-*g*-GMA copolymer used by Tedesco et al. [38] for PP/PA blends, it was nevertheless lower than expected. In agreement with the conclusions of Kudva et al. [37], we believe that this may be due to the high reactivity of the epoxy groups of EGMA with both the amine and the carboxyl groups of PA and to the possible formation of loops or bridge structures which cause the agglomeration of the PA particles.

4. Conclusions

The characterization of the binary LD08/EGMA and LD03/EGMA blends has shown that LDPE and EGMA are not miscible, yet physically compatible and mutually adherent. The investigation of the PA/EGMA blends has demonstrated that the epoxy groups of this CP are capable of reacting with both the amine and the carboxyl end groups of PA, and may even lead to cross-linked products if the two polymers are blended in appropriate proportions. The PA-*g*-EGMA copolymers produced when blending the two polymers at 235 °C could be separated by solvent fractionation from the binary blends, and their composition was determined through calorimetric and gravimetric measurements carried out on the blends and their fractions. By the use of an appropriate solvent mixture, it was demonstrated that these copolymers are in fact partially cross-linked, whereas those produced by blending PA with the EAA copolymers [16] or with MA-functionalized polyethylenes [17] are completely soluble.

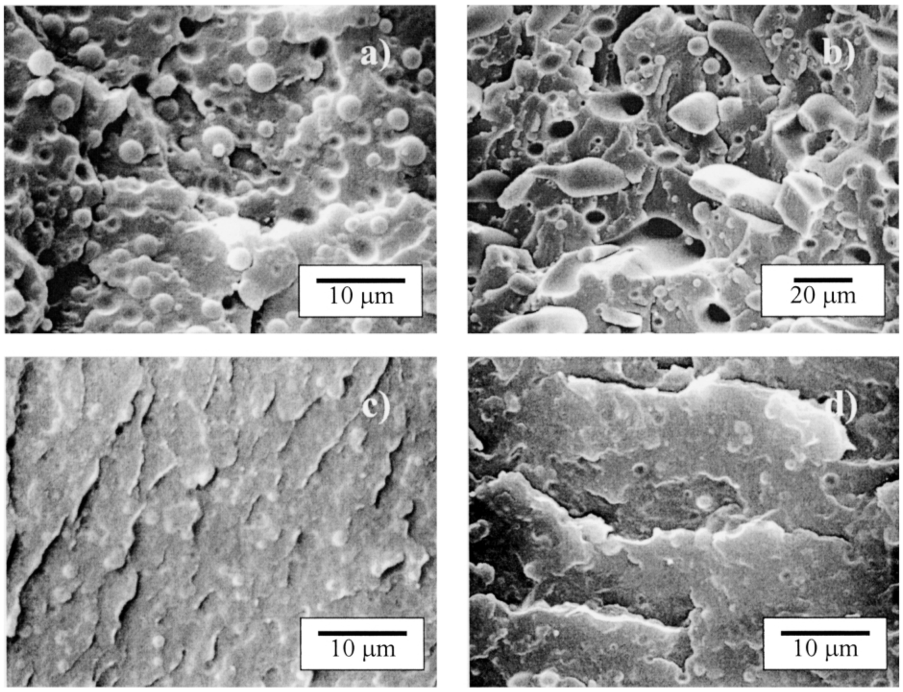


Fig. 5. SEM micrographs of the cryofractured surfaces of the 75/25 LD08/PA ((a), (c)) and LD03/PA ((b), (d)) blends, without ((a), (b)) and with ((c), (d)) 2 phr EGMA.

The blends of PA with LD08 or LD03, with and without compatibilizer, have been studied in the whole composition range by dynamic and isothermal calorimetry and electron microscopy. The effectiveness of EGMA as a reactive compatibilizer was found to be comparable to that of the EAA copolymers, yet lower than that of a particular MA-functionalized PE that was studied in a previous work. The latter result, which was somewhat unexpected, given the

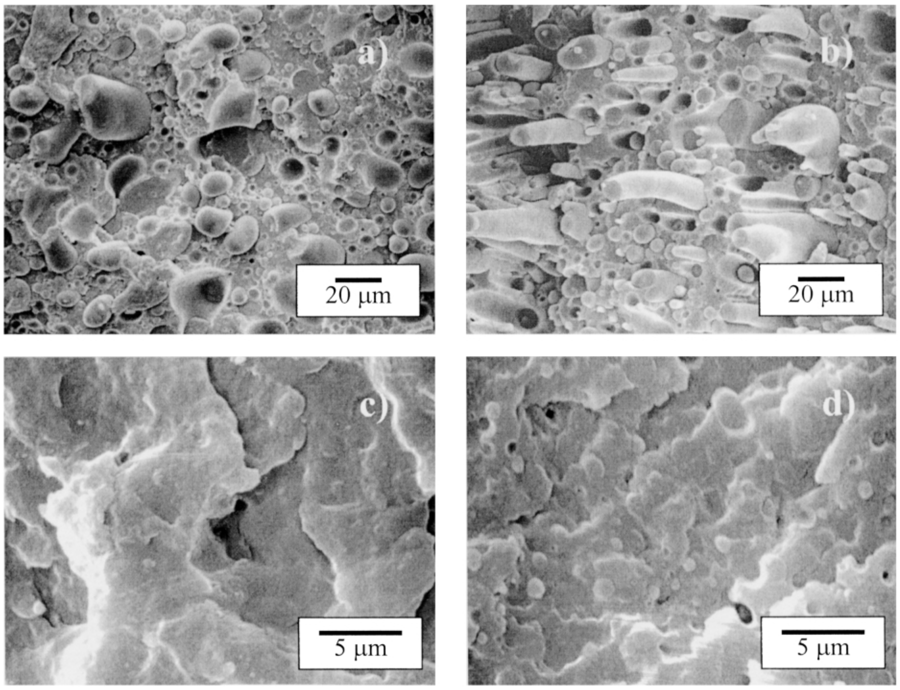


Fig. 6. SEM micrographs of the cryofractured surfaces of the 40/60 LD08/PA ((a), (c)) and LD03/PA ((b), (d)) blends, without ((a), (b)) and with ((c), (d)) 2 phr EGMA.

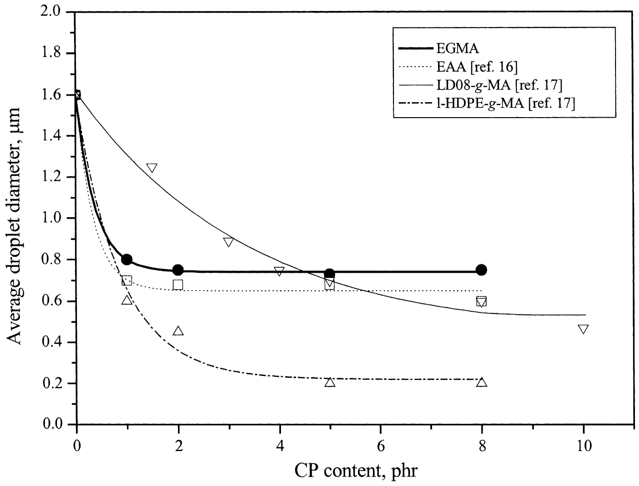


Fig. 7. Emulsification curves for the 75/25 LD08/PA blends compatibilized with different CPs: EGMA, EAA [16], LD08-*g*-MA [17], and l-HDPE-*g*-MA [17].

high reactivity of the epoxy groups, was ascribed to the possible formation of PA-*g*-EGMA copolymers containing bridge structures which may lead to agglomeration of the PA droplets.

Acknowledgements

This work was financially supported by the Italian Ministry of University and Scientific and Technological Research (MURST), contract no. MM09244737. The contribution of CNR and BAN (co-operation agreement between the Consiglio Nazionale delle Ricerche and the Bulgarian Academy of Sciences) is also gratefully acknowledged. Thanks are due to Polimeri Europa, Snia Tecnopolimeri and Elf-Atochem for providing samples of the polymers used in this work.

References

[1] Datta S, Lohse DJ. Polymeric compatibilizers: uses and benefits in polymer blends. Munich: Hanser; 1990.
[2] Akkapeddi MK, Van Buskirk B, Mason CD, Chung SS, Swamikannu X. Polym Engng Sci 1995;35:72–8.
[3] Armat R, Moet A. Polymer 1993;34:977–85.
[4] Chandramouli K, Jabarin SA. SPE Antec 1993;2111–9.
[5] Beltrame PL, Castelli A, Di Pasquantonio M, Canetti M, Seves A. J Appl Polym Sci 1996;60:579–90.
[6] Gadekar R, Kulkarni A, Jog JP. J Appl Polym Sci 1998;69:161–8.
[7] Chen JC, Harrison IR. Polym Engng Sci 1998;38:371–83.
[8] Yao Z, Yin Z, Sun G, Liu C, Tong J, Ren L. J Appl Polym Sci 2000; 75:232–8.
[9] Raval H, Devi S, Singh YP, Mehta MH. Polymer 1991;32:493–500.
[10] Valenza A, Geuskens G, Spadaro G. Eur. Polym J 1997;33:957–62.
[11] Geppi M, Forte C, Passaglia E, Mendez B. Macromol Chem Phys 1998;199:1957–63.
[12] Yeh JT, Fan-Chiang CC. J Appl Polym Sci 1997;66:2517–27.
[13] Yeh JT, Jyan CF. Polym Engng Sci 1998;38:1482–90.
[14] Sheng J, Ma H, Yuan XB, Yuan XY, Shen NX, Bian DC. J Appl Polym Sci 2000;76:488–94.
[15] Vocke C, Anttila U, Seppäla J. J Appl Polym Sci 1999;72:1443–50.
[16] Filippi S, Chiono V, Polacco G, Paci M, Minkova L, Magagnini PL. Macromol Chem Phys 2002;203:1512–25.
[17] Jiang C, Filippi S, Magagnini P. Submitted for publication.
[18] Dagli S, Kamdar K. Polym Engng Sci 1994;34:1709–19.
[19] Pazzagli F, Pracella M. Macromol Symp 2000;149:225–30.
[20] Loyens W, Groeninckx G. Macromol Chem Phys 2002;203(10/11): 1702–15.
[21] Loyens W, Groeninckx G. Polymer 2002;43:5679–91.
[22] Gallucci RR, Going RC. J Appl Polym Sci 1982;27:425–37.
[23] Hert M. Angew Makromol Chem 1992;196:89–99.
[24] Stewart ME, George SE, Miller RL, Paul DR. Polym Engng Sci 1993; 33:675–85.
[25] Holsti-Miettinen RM, Heino MT, Seppäla J. J Appl Polym Sci 1995; 57:573–80.
[26] Moffett AJ, Dekkers MEJ. Polym Engng Sci 1992;32:1–5.
[27] Campbell JR, Khouri FF, Hobbs SY, Shea TJ. Polym Prep 1993;34: 846–7.
[28] Chang FC, Hwu YC. Polym Engng Sci 1991;31:1509–19.
[29] Zhang X, Li XL, Wang D, Yin Z, Yin J. J Appl Polym Sci 1997;64: 1489–98.
[30] Koulouri EG, Georgaki AX, Kallitsis JK. Polymer 1997;38:4185–92.
[31] Shechter J, Wynstra J. Ind Engng Chem 1956;48:94–7.
[32] Iwakura Y, Kurosaki T, Ariga N, Ito T. Makromol Chem 1966;97: 128–38.
[33] Kalal J, Svec F, Marousek V. J Polym Sci. Polym Symp 1974;47: 155–66.
[34] Duffy JV, Hui E, Hartmann B. J Appl Polym Sci 1987;33:2959–64.
[35] Glover D, Duffy JV, Hartmann B. J Polym Sci Part A Polym Chem 1988;26:79–87.
[36] Shechter J, Wynstra J. Ind Engng Chem 1956;48:86–93.
[37] Kudva RA, Keskkula H, Paul DR. Polymer 1998;39:2447–60.
[38] Tedesco A, Barbosa RV, Nachtigall SMB, Mauler RS. Polym Test 2002;21:11–15.
[39] Molau GE. Kolloid Z Z Polym 1970;238:493–8.
[40] Illing G. Angew Makromol Chem 1981;95:83–108.
[41] Minkova L, Yordanov Hr, Filippi S. Polymer 2002;43:6195–204.