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Reactive blending of commercial PET and PC with freshly added catalysts

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Reactive blending of commercial poly(ethylene terephthalate) (PET) and bisphenol A polycarbonate (PC), with catalysts added in the form of powder dispersed on the polymers just before melt mixing, was performed in a Brabender Plasticord 2000 apparatus at 275°C. Catalytic activity of the catalysts freshly added to polymers was found to be much higher as compared with that of the residues of the same type of catalysts remaining in PET after its synthesis. Furthermore, the catalytic activity appeared to be strongly dependent on the structure of the ligand that influences the catalyst solubility in the polymer melt. N.m.r. spectroscopy, selective degradation of PC fragments, solubility tests in methylene chloride and d.s.c. measurements made it possible to range the catalysts studied according to their catalytic activity. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Results reported in a series of papers[1-13] dedicated to poly(ethylene terephthalate)/bisphenol A polycarbonate (PET/PC) reactive blending allowed us to consider this method as one of the most prospective techniques for production of new polymer materials based on polyesters and polycarbonates. Residues of catalysts in commercial PET (calcium acetate/antimony oxide) were found to possess very low catalytic activity towards exchange reactions in the PET/PC melt and to be less effective in the formation of compatible blends. On the other hand residues of titanium tetrabutoxide led to very fast exchange reactions and side processes with degradation of aliphatic carbonate fragments, liberation of carbon dioxide and cyclic ethylene carbonate[4].

Lanthanide compounds employed for PET synthesis and its further reactive blending with PC[8-11] appeared to possess intermediate activity towards exchange reactions. The contribution of side reactions was found to be rather low as compared with that of the Ti catalyst. This provided a possibility for producing PET/PC block copolymers and employing them as compatibilizers for PET/PC blends[9-13].

It should be noted that in all cases mentioned above exchange reactions were induced by the residual polycondensation catalyst in the PET, which can change its activity during and after PET synthesis. Thus, the same catalyst is supposed to have different activity, when dispersed in PET or PC before their blending, as compared to the residue in PET, because it is freshly added and concentrated on the polymer surface, where the exchange reactions occur.

Some results of PET/PC melt mixing in the presence of lanthanide and other catalysts, dispersed on polymers before their blending in a Brabender Plasticord 2000 apparatus, are presented in this paper.

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EXPERIMENTAL

Materials

Samples of PET ($[\eta] = 0.65\,\mathrm{dl\,g}^{-1}$ in 1,1,2,2-tetra-chloroethane/phenol, 60/40 wt/wt, at 25°C) and PC ($[\eta] = 0.61\,\mathrm{dl\,g}^{-1}$ in the same solvent at 25°C) were commercial products supplied by EniChem S.p.A., Italy. PET ($[\eta] = 0.91\,\mathrm{dl\,g}^{-1}$ in the same solvent) was synthesized in the presence of $Ti(OBu)_4$ (0.066 mol% with respect to PET units) by a standard procedure[12]. Polymers, before using, were dried overnight in a vacuum oven at 120°C before use. Lanthanum acetyl acetonate ($La(acac)_3 \cdot xH_2O$ ($x = 3$–4)), $Al(acac)_3$, Sm $(ac)_3 \cdot xH_2O$ ($x = 3$–6), $Zn(ac)_2 \cdot 2H_2O$ and $Ti(OBu)_4$ were purchased from Aldrich and used without further purification. $Sm(acac)_3 \cdot xH_2O$ ($x = 3$–4), $Ca(acac)_2 \cdot 2H_2O$, $Zn(acac)_2 \cdot 2H_2O$, $Pb(acac)_2 \cdot 2H_2O$, $Ba(acac)_2 \cdot 2H_2O$, $Sr(acac)_2 \cdot 2H_2O$ and Sm(o-formyl phenolate)$_3$ were synthesized by a standard technique as described before[12].

Syntheses of lanthanum oxalate, tartrate, phthalimide and samarium phthalates

An aqueous solution of La or Sm chloride (5–6%) was gradually poured into the aqueous solution of potassium oxalate, tartrate, phthalimide or phthalate (5–6%). The precipitated product was separated by centrifugation, then dried in a vacuum oven at 40°C overnight. All products were characterized by i.r. spectroscopy and elemental analysis.

PET/PC reactive blending

A Brabender Plasticord 2000 mixer equipped with two counter-rotating, double-winged rotors was used for the melt mixing. A PET/PC mixture (50/50, wt/wt) in a total amount of 50 g was loaded into the mixing bowl under a moderate nitrogen flux, and mixed at a temperature of 275°C and rotation rate for 48 rev min^{-1} throughout the overall reaction time. A catalyst (when used) was initially dispersed mechanically on polymer pellets at a concentration of 0.066 mol% with respect to PET units (for all catalysts employed). This concentration corresponded to that of the catalysts used in the PET synthesis[7–11]. After a definite time of blending the product was unloaded manually into cold water, ground into fine powder and dried *in vacuo* overnight.

Measurements

Intrinsic viscosity values were calculated on the basis of viscosity measurements of dilute solutions of the samples in tetrachloroethane/phenol mixture (60/40, wt/wt) at 25°C.

Crystallization and melting temperatures (T_c and T_m, respectively) were calculated on the basis of thermograms of the first scanning of quenched samples obtained with a DSC 7 Perkin-Elmer instrument (50–300°C, 20°C min^{-1}, under nitrogen).

The ^1H n.m.r. spectra of the PET/PC block copolymers dissolved in $CDCl_3/CF_3CO_2D$ (85/15, wt/wt) were recorded on a Bruker AMX 300 instrument.

Solubility tests of the samples ground to fine powders were performed in a Soxhlet apparatus with methylene chloride for 48 h.

Selective degradation of the PC fraction in PET/PC blends and copolymers was performed with piperidine in methylene chloride as described elsewhere[4,11]. This method provides a possibility for evaluating the length of PET segments in the resulting PET/PC blends and copolymers.

RESULTS AND DISCUSSION

As we reported in our previous papers[4–6], residues of catalysts in commercial PET were found to be insufficiently active in exchange reactions in the PET/PC melt to provide formation of compatible blends for a short reaction time. On the other hand, residues of $Ti(OBu)_4$ in PET led to very fast exchange reactions and side processes that resulted in the formation of copoly(ether ester carbonate)s. Lanthanide compounds employed for PET synthesis and its further reactive blending with PC appeared to possess intermediate activity towards exchange reactions[7–12], and the contribution of side reactions was found to be rather low as compared with that of the Ti catalyst. It should also be noted that lanthanide compounds have shown a wide range of catalytic activity, depending on the metal employed. In all the above cases the catalyst was that used for the PET synthesis, which remains still active during the blending with PC. Because the exchange reactions between PC and PET occur at the interface, only a small fraction of the overall amount of catalyst present in PET is believed to be initially active in such a system. Therefore, the next step in our study was the investigation of catalytic behaviour of lanthanides mechanically dispersed in commercial PET and PC just before their blending; by this procedure all the catalyst is initially present on the granule surface and it is expected to work more efficiently. A first qualitative evaluation of the difference in catalytic activities of the lanthanide residues in PET and the fresh catalysts added to commercial polymers can be made on the basis of the torque values recorded during reactive blending, and data for the solubility of the resulting products in methylene chloride. As was reported before[10,11], for most cases the torque increases in the first period of exchange reactions, goes through a maximum, then decreases until a constant level or increases slowly again. It can be assumed that the torque profile in all cases reflects the extent of the reaction regardless of the type of the catalyst.

As has been established, the maximum of the torque was recorded in 16–18 min of blending of the neat PET/PC system, containing just residual catalysts in commercial PET; while it appeared in 8 min of PC blending with PET synthesized in the presence of $Sm(acac)_3$. However, introduction of the same catalyst added in the form of powder dispersed on pellets of commercial PET and PC just before melt mixing reduces the time of the torque maximum to 2.5 min; this indicates much higher catalytic activity of the fresh catalyst as compared with the activity of the same amount of catalyst used for the PET synthesis and present as a residue.

Data for the solubility of the resulting blends in methylene chloride can also be used for preliminary evaluation of catalytic activity of the catalysts employed (*Figure 1*). Since PET is absolutely insoluble in that solvent, and PC is found to be completely soluble, the decrease of the initial value of the soluble fraction (50%, corresponding to the neat PC fraction) indicates the process of block copolymer formation.

The minimum of the solubility of the blends of commercial PET and PC was reached in 80–90 min of
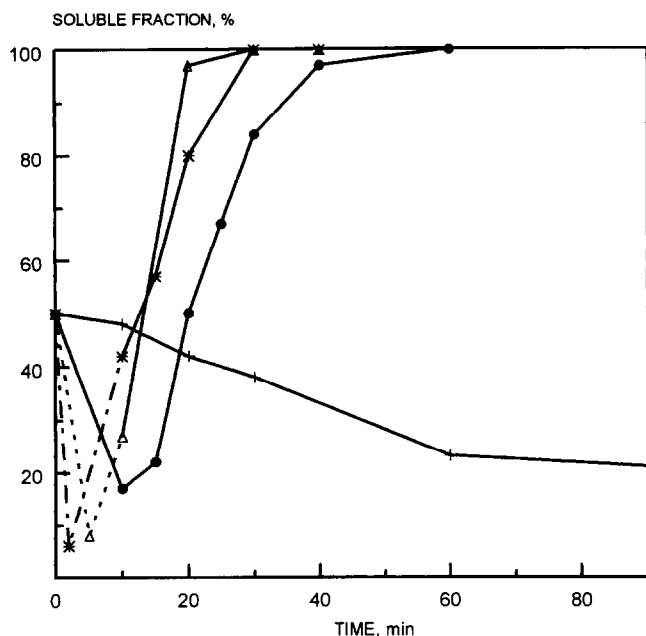
SOLUBLE FRACTION, %

Figure 1 Solubility tests of PET/PC blends obtained by reactive blending in a Brabender at 275°C. Curve 1: neat mixture of commercial PET and PC (+); curve 2: blends of PC with PET synthesized with Sm(acac)₃, 0.066 mol% with respect to PET units (●); curve 3: blends of commercial PET and PC obtained with Sm(acac)₃ added before blending, 0.066 mol% with respect to PET units (*); curve 4: blends of PC with PET synthesized with Ti(OBu)₄, 0.66 mol% with respect to PET units (△)

blending (*Figure 1*, curve 1), while in the case of PET synthesized with Sm(acac)₃ this time was reduced to 10 min (curve 2). When the same catalyst was distributed on polymers just before blending the value for the solubility in 10 min was found to be 40% and this value then increased sharply to 100% (curve 3). Unfortunately, we could not observe a minimum in the solubility curves because it was technically impossible to reach the required temperature regime of blending after polymer loading for a time less than 10 min. In any case, curve 3 is very similar to that obtained for the blends of PC and PET with residual Ti(OBu)₄ (curve 4). This reveals that the catalytic activity of freshly added Sm(acac)₃ in the first step of the exchange reactions is the same or even higher than that of residues of Ti catalyst remaining in the PET. From the latter two curves (3 and 4) we can estimate a hypothetical minimum of solubility at 2–4 min. It should be noted that some equilibrium between formation of block copolymers and their further shortening because of exchange reactions does not allow one to obtain completely insoluble systems.

We examined also the effect of Ti(OBu)₄, being introduced into the mixture of commercial PET and PC before their blending. Surprisingly, we found that it was less active as compared to its residues in PET synthesized with Ti(OBu)₄. This could be caused by side reactions with impurities and commercial stabilizers in PET.

Sm(acac)₃ freshly added to polymers and residues of Ti(OBu)₄ in PET show similar catalytic activity with respect to the reaction rate; nevertheless, they lead to formation of copolymers with quite different chemical structure and composition. Selective degradation of PC moieties in the samples blended for 10 min revealed that in the case of the Ti catalyst the viscosity value of PET
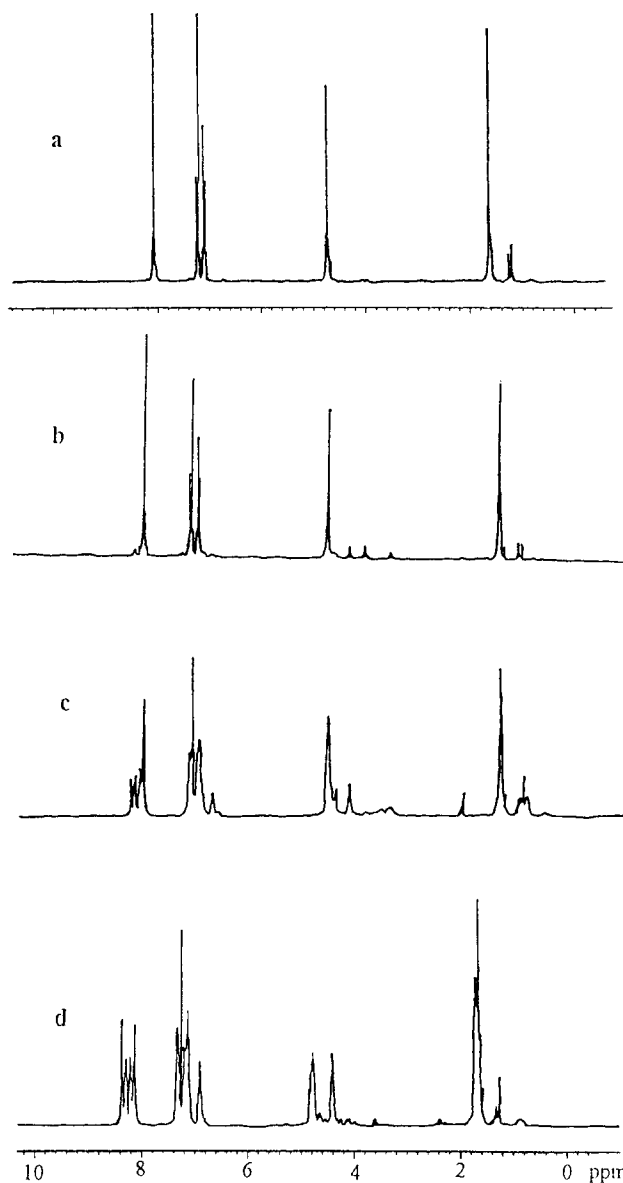

Figure 2 ¹H n.m.r. spectrum of the neat PET/PC mixture (a) before blending, and blends of PC with PET synthesized with Ti(OBu)₄ in (b) 10 min, (c) 30 min and (d) 60 min of melt blending in a Brabender at 275°C and 48 rev min⁻¹

segments decreased dramatically (by a factor of 10) from the initial value of 0.91 to 0.09 dl g⁻¹, while Sm(acac)₃, being added to commercial PET and PC, did not lead to so drastic scission of PET blocks. The viscosity value of PET segments in the latter case decreased by a factor of four (from 0.65 to 0.17 dl g⁻¹).

One of the most appropriate techniques for investigation of the chemical structure of the reactive blends and copolymers is ¹H n.m.r. spectroscopy. Application of this technique for studying PET/PC blends was described earlier[2-6]. Exchange reactions in the blend of PC with PET synthesized with Ti catalyst result finally in formation of a random copoly(ether ester carbonate) because of side reactions, leading to elimination of carbon dioxide and cyclic ethylene carbonate, which enriches the final structure of the product with aromatic fragments. The process above is reflected in the spectra (*Figures 2a–d*). If before reactive blending a single peak at 8.08 ppm, corresponding to the terephthalate protons, was observed, other signals assigned to aromatic
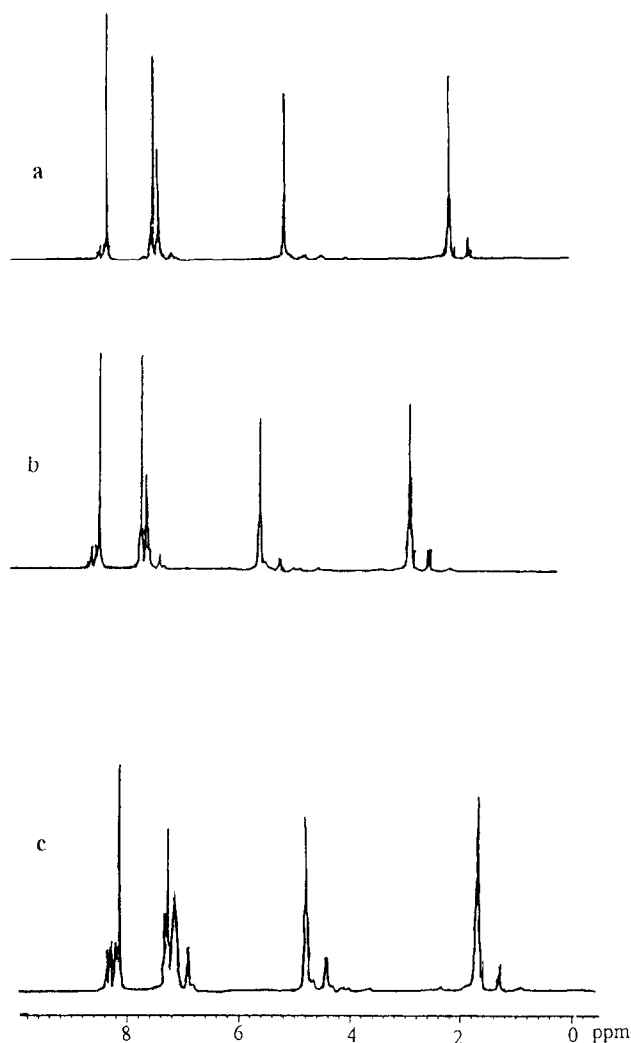
Figure 3 ^{1}H n.m.r. spectrum of the products of reactive blending of commercial PET and PC in the presence of Sm(acac)$_3$ after (a) 10 min, (b) 30 min and (c) 60 min of blending

hetero- and homo-triads of terephthalic fragments appeared in the range 8–8.4 ppm during reactive blending for 10–60 min. Formation of ether groups is more clearly observed in the region of aliphatic ethylene protons, where a new peak assigned to the ethylene protons adjacent to ether groups appears at 4.41 ppm. Appearance of the signal at 6.9 ppm assigned to the aromatic protons of bisphenol A fragments adjacent to ether groups confirms the structure of copoly(ether ester carbonate) formed in the presence of Ti residues. Meanwhile, much weaker signals, corresponding to ether groups, appear in the spectra of the resulting products of PET/PC melt blending in the presence of Sm(acac)$_3$ for the same reaction time (*Figures 3a–c*).

The reason for the higher activity of lanthanide catalyst introduced into the PET/PC system as compared with residues of the same catalyst in PET, remaining after its synthesis, can be explained by the interfacial character of exchange reactions during the melt blending. When the catalyst is introduced before reactive blending, exchange reactions take place at the interface between two phases of immiscible polymers where the catalyst concentration is much higher as compared with the average concentration of the residues of the same catalyst distributed within the PET phase. Being added, catalyst is concentrated in the polymer surfaces, providing a higher rate of exchange reactions.

Another reason for the higher activity of the same catalyst added before reactive blending could be its freshness as compared with that of the residual catalyst used for PET synthesis.

Some other catalysts, being added before reactive blending, were found to possess catalytic activity towards exchange reactions as well. Data for the torque maximum, solubility, T_c and T_m of the samples blended for 10 min are presented in *Table 1*. It should be noted that the d.s.c. method, being very sensitive, as seen especially from the data for T_c, reflects even first interchain reactions, when the degree of conversion of exchange reaction is very low.

Table 1 Reactive blending of PET/PC (1/1, wt/wt) in Brabender at 275°C, 48 rev min^{-1}, in the presence of various catalysts (0.066 mol% with respect to PET units) freshly added to polymer before blending

| Catalyst | Time to the torque max. (min) | Soluble fraction | | Slope and direction of the solubility curve[a] | T_c (°C) (d.s.c.)[b] | T_m (°C) (d.s.c.)[b] |
		10 min (%)	20 min (%)			
Without catalyst	16	48	42	↓ Slow down	144	248
Sm(ac)$_3$	12	47	38	↓ Slow down	147	241
Sm(phthalate)$_3$	16	49	44	↓ Slow down	146	239
Sm(acac)$_3$	2,5	40	80	↑ Speed up	Not observed	Not observed
Sm(o-formyl phenolate)$_3$	3,8	35	100	↑ Speed up	Not observed	Not observed
La$_2$(oxalate)$_3$	16	49	43	↓ Slow down	143	249
La$_2$(tartrate)$_3$	14	49	42	↓ Slow down	145	238
La$_2$(phthalimide)$_3$	14	47	37	↓ Slow down	159	242
La(acac)$_3$	4	21	74	↑ Speed up	Not observed	Not observed
Al(acac)$_3$	6,5	15	53	↑ Up	193	230
Ca(acac)$_2$	9	40	27	↓ Down	170	236
Sr(acac)$_2$	8	37	22	↓ Down	168	237
Ba(acac)$_2$	6	14	56	↑ Up	189	231
Zn(acac)$_2$	8	39	25	↓ Down	176	236
Zn(ac)$_2$	7	38	26	↓ Down	157	238

[a] See *Figure 1*
[b] For the samples obtained by blending for 10 min

Further exchange reactions lead to randomization of PET/PC block copolymers and formation of amorphous copolymers. In the case of the most active catalysts, T_c and T_m were not observed under the conditions of d.s.c. measurements (see Experimental section).

To consider the solubility data presented in *Table 1* it is necessary to take into account that some of these data lie on two different shoulders of the curve, initially going down and then running up to the plateau at 100% of solubility (*Figure 1*).

Carboxylic acid salts of lanthanides appeared to possess very low catalytic activity (samarium phthalate and acetate; lanthanum oxalate, tartrate and phthalimide), while the complexes with bidentate ligands (acetyl acetonates and *o*-formyl phenolate) show high efficiency. Probably, the latter ligands just provide enough solubility of the catalysts in the PET/PC melt, where carboxylic acid salts were found to be less soluble. In the samples obtained with acetyl acetonates of lanthanum and samarium, and also with samarium *o*-formyl phenolate, crystallization and melting temperatures are no longer observed.

Zinc compounds were found to be less active regardless of the structure of the ligand (acetates or acetyl acetonates). The catalytic activity of acetyl acetonates of the alkaline earth metals (Ca, Sr and Ba) increased with increase in the atomic number of the metal. Aluminum acetyl acetonate proved to be a quite efficient catalyst as well.

All the catalysts employed can be ordered in the following activity rank: $Sm(acac)_3 = Sm(formyl\ phenolate)_3 > La(acac)_3 > Al(acac)_3 = Ba(acac)_2 > Zn(acac)_2 = Zn(ac)_2 > Sr(acac)_2 = Ca(acac)_2 > La(phthalimide)_3 > La_2(tartrate)_3 > La_2(oxalate)_3 = Sm(phthalate)_3 = Sm(ac)_3$ = residues of commercial catalysts in PET.

CONCLUSIONS

- On the basis of the results above we can conclude that the catalytic activity of lanthanides added to a neat mixture of commercial PET and PC before reactive blending is much higher towards exchange reactions than that of the residues of the same type of catalysts, remaining in PET after its synthesis. The effect of the catalyst on the extent of exchange reactions depends also on the nature of the ligands that can influence the solubility in the PET/PC system.

- The contribution of side reactions (degradation of carbonate groups, release of carbon dioxide and cyclic ethylene carbonate) in the presence of lanthanides is much lower as compared with the effect of the Ti catalyst.

- Alkaline earth metals were found to possess some catalytic activity in exchange reactions, which increases with the increase in atomic number of the metal.

- Since the higher intensity of melt mixing can promote interfacial exchange reactions, application of a twin-screw extruder, providing higher intensity of mixing and shear rate as compared with that of the Brabender apparatus, would be of interest. Preparation of polyester/polycarbonate blends and copolymers by one-step extrusion will be the subject of our further publications in this journal.

REFERENCES

1   Porter, R. S. and Wang, L. H. *Polymer* 1992, **23**, 2019
2   Godard, P., Dekoninck, J. M., Devlesaver, V. and Devaux, J. *J. Polym. Sci., Polym. Chem.* 1986, **24**, 3301
3   Godard, P., Dekoninck, J. M., Devlesaver, V. and Devaux, J. *J. Polym. Sci., Polym. Chem.* 1986, **24**, 3315
4   Pilati, F., Marianucci, E. and Berti, C. *J. Appl. Polym. Sci.* 1985, **30**, 1267
5   Berti, C., Bonora, V. and Pilati, F. *Makromol. Chem.* 1992, **193**, 1665
6   Berti, C., Bonora, V. and Pilati, F. *Makromol. Chem.* 1992, **193**, 1686
7   Berti, C., Bonora, V., Fiorini, M. and Pilati, F. Preprints of the Italian–Russian Joint Meeting in Polymer Science, AIM Torino, Italy, 1993, p. 24
8   Nadali, G. P., Tartari, V., Ignatov, V. N., Fiorini, M. and Bonora, V. Patent Pending, EniChem (filed May 1993)
9   Nadali, G. P., Tartari, V., Ignatov, V. N., Pilati, F., Berti, C. and Fiorini, M. Patent Pending, EniChem (filed May 1993)
10   Pilati, F., Berti, C., Fiorini, M., Toselli, M., Ignatov, V. N., Pippa, R., Tartari, V., Carraro, C. and Moro, A. Abstracts of the 6th International Symposium on Polymer Supported Reactions in Organic Chemistry, University of Venice, 1994, p. 146
11   Fiorini, M., Berti, C., Ignatov, V. N., Toselli, M. and Pilati, F. *J. Appl. Polym. Sci.* 1995, **55**, 1157
12   Ignatov, V. N., Pilati, F., Berti, C., Tartari, V., Carraro, C., Nadali, G. P., Fiorini, M. and Toselli, M. *J. Appl. Polym. Sci.* 1995, **58**, 771
13   Fiorini, M., Berti, C., Ignatov, V., Nadali, G. P., Pilati, F., and Toselli, M. Preprints of the Fourth European Symposium on Polymer Blends, 1993, Capri, Italy, p. 173