

Modification of Acrylonitrile–Butadiene–Styrene Terpolymer by Grafting with Maleic Anhydride in the Melt. I. Preparation and Characterization

Rongrong Qi, Junling Qian, Chixing Zhou

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

Received 5 September 2002; accepted 6 December 2002

ABSTRACT: The graft copolymerization of maleic anhydride (MAH) onto acrylonitrile–butadiene–styrene terpolymer (ABS) was carried out with dicumyl peroxide (DCP) and benzoyl peroxide (BPO) as the binary initiators and with styrene as the comonomer in the molten state. IR spectra confirmed that MAH was successfully grafted onto the ABS backbone. A reaction mechanism was proposed: the grafting most likely took place through the addition of MAH radicals to the double bond of the butadiene region of ABS. Influ-

ences such as the MAH concentration, the initiators and their concentrations, the reaction temperature, the rotating speed, and the comonomer concentration were studied. The results indicated that using styrene as a comonomer and DCP/BPO as binary initiators was beneficial for the graft copolymerization. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1249–1254, 2003

Key words: graft copolymers; initiators; monomers

INTRODUCTION

Polymer blending is an effective way of achieving improved properties generally not available in any single polymeric material, such as toughness, chemical resistance, and ease of fabrication.¹ Polymers are usually incompatible, and so the properties of blends are generally poor because of very high interfacial tension between the two phases. A common way of compatibilizing polymer blends is adding a compatibilizer to reduce the interfacial tension, increase the adhesion, and obtain better properties.² Functionalized polymers are used as compatibilizers in the reactive compatibilization of polymer blends³ and can be obtained by the graft copolymerization of functional monomers with existing polymers. Graft polymerization can be initiated by various methods, such as high energy (γ rays and electron beams),^{4,5} plasma treatment,⁶ ultraviolet,^{7,8} chemical initiators (including graft polymerization in solution and in melt), and polymer oxidation. Methacrylic acid,⁹ styrene,^{10–13} acrylic acid,¹⁴ benzyl acrylate,¹⁵ maleic anhydride (MAH),¹⁶ glycidyl methacrylate, acryl amide,¹⁷ oxazoline,^{2,18} and long-chain unsaturated monomers^{19,20} are among the monomers most commonly grafted onto polymers containing butadiene. Several articles^{7,8,14,16,17,19,20} have recently appeared on the subject of the grafting of vinyl monomers onto acrylonitrile–butadiene–sty-

rene terpolymer (ABS). In comparison with solution grafting, melt grafting is more convenient and effective for industry, but the grafting degree (GD) obtained by this method is usually low.

In a previous works on the graft copolymerization of MAH onto ABS, only MAH and benzoyl peroxide (BPO), azobisisobutyronitrile, or dicumyl peroxide (DCP) were used, and a low GD was obtained. For improvement in the GD, the graft copolymerization of MAH onto ABS was carried out with DCP and BPO as a binary initiator and with styrene as a comonomer in the molten state. The influences of the MAH concentration, the initiators and their concentrations, the reaction temperature, the rotation speed, and the comonomer concentration were also studied.

EXPERIMENTAL

Materials

ABS was purchased from Taiwan Qimei Co., Ltd. (Taiwan, China) (number-average molecular weight = 49,000, weight-average molecular weight = 134,000, weight-average molecular weight/number-average molecular weight = 2.72; 2.7 wt % additives, 22.4 wt % acrylonitrile, 13.5 wt % butadiene, and 61.4 wt % styrene, as determined by elemental analysis and solvent separation). BPO (Shanghai Lingfeng Chemical Solvent Factory, Shanghai, China) was purified by dissolution in chloroform at room temperature and precipitation in cool methanol. DCP and MAH (Shanghai Chemical Solvent Factory) were used without further purification. Styrene was purified by distillation under reduced pressure at 30°C.

Correspondence to: R. Qi (rrqi@sjtu.edu.cn).

Synthesis of the grafted copolymers

Grafting was carried out in the molten state with a Haake twin-screw extruder (Germany) under various processing conditions. ABS, MAH, initiators, a solvent, and, in some tests, comonomers were simultaneously introduced into the twin-screw extruder after dry blending. The obtained product was dissolved in 1,2-dichloroethane, and then unreacted MAH was extracted with ethanol. The purified polymer was collected and dried to a constant weight in a vacuum oven at 80°C.

Characterization

The samples were cast into films (0.010–0.015 mm thick) with chloroform as a solvent. IR spectroscopy information on ABS and grafted ABS was obtained with a PerkinElmer Paragon 1000 Fourier transform infrared (FTIR) spectrophotometer (USA). No significant changes were observed in the FTIR spectrum of the grafted ABS after further purification, and this indicated that the procedure was effective.

Determination of the GD of MAH

The GD of MAH was determined by a back-titration procedure. The purified sample (1.0 g) was dissolved in 100 mL of acetone, and then 10 mL of an ethanol solution of NaOH (0.1 mol/L) was added. The mixed solution was refluxed for 30 min with stirring and then back-titrated with 0.1 mol/L HCl with methyl red as an indicator.

GD was defined as the amount of grafted MAH as a percentage of ABS:

$$\text{GD (\%)} = \frac{(V_0 - V_1) \times 10^{-3} \times C \times M}{2W} \times 100$$

where V_0 is the amount of HCl consumed with pure ABS as a reference (mL), V_1 is the amount of HCl consumed by the grafted sample (mL), C is the molar concentration of HCl (mol/L), M is the molecular weight of MAH, and W is the weight of the sample (g).

Phase separation of ABS and grafted ABS

For further information on the ABS-g-MAH copolymer, the obtained copolymer was separated into three fractions with a solvent fractionation method similar to Gesner's.²¹ Pure ABS was first dissolved in 1,2-dichloroethane and precipitated in ethanol to give the polymer as a fine powder; 1.0 g of this fine powder of ABS or grafted ABS was refluxed in 200 mL of cyclohexane for 2 h with stirring, after which the solid residue was filtered from the hot cyclohexane solution. The cyclohexane extract was evaporated to dry-

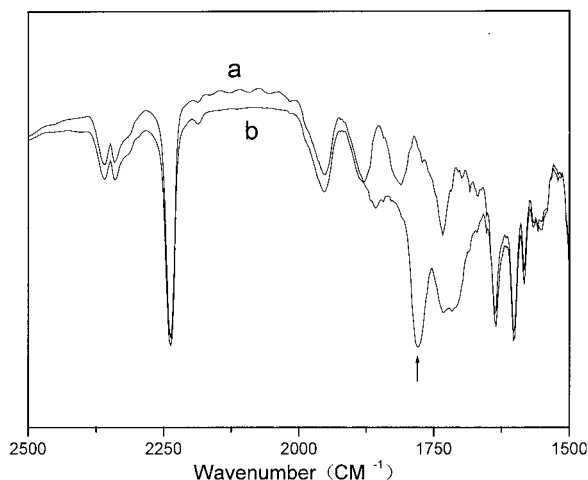


Figure 1 FTIR spectra of (a) ABS and (b) ABS-g-MAH.

ness under a purge of N_2 . The residue was weighed, redissolved in cyclohexane, and spun on a KBr salt plate for FTIR analysis. The cyclohexane-insoluble material was stirred in 200 mL of cold acetone for 2 h and centrifuged at 30,000 rpm for 2 h. The supernatant liquid was removed and cast into a thin film for FTIR analysis. The acetone-insoluble material in the centrifuge tube was weighed and sandwiched with KBr for FTIR.

RESULTS AND DISCUSSION

Characterization of grafting

Figure 1 shows the IR spectra of ABS and grafted ABS. Different from the IR spectrum of pure ABS, the spectrum of grafted ABS showed a new absorbance peak at 1780 cm^{-1} ($C=O$ stretching from anhydride), which indicated that MAH was successfully introduced onto ABS.

For more information on the ABS-g-MAH copolymer, the IR spectra of three fractions from solvent separation are shown in Figure 2. The cyclohexane-soluble fraction was free PB and/or free polybutadiene (PB) grafted with MAH; the cyclohexane-insoluble but acetone-soluble fraction was styrene-acrylonitrile (SAN) copolymer, and the acetone-insoluble fraction was grafted copolymer and/or crosslinked PB. As shown in Figure 2, no MAH was grafted onto SAN, but grafting did occur in cyclohexane-soluble and acetone-insoluble fractions. Therefore, the grafting of MAH most likely took place in the butadiene region of ABS, and this agreed with the results of Chandrasiri and Wilkie.¹⁴

Effect of the initiator

As for the graft copolymerization of MAH onto ABS, the reaction proceeded as a typical radical polymer-

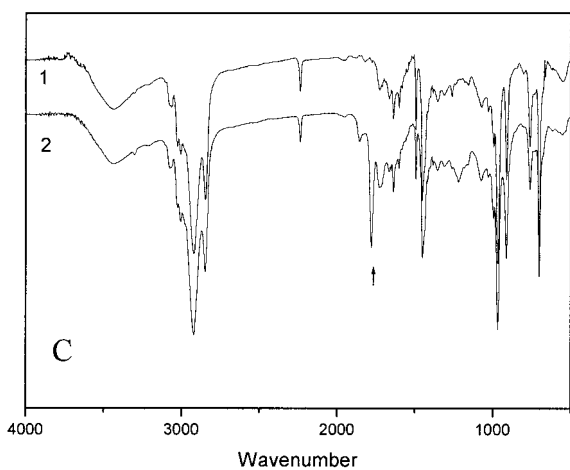
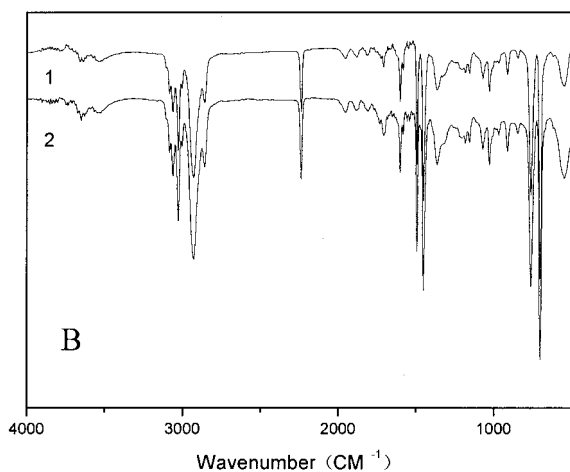
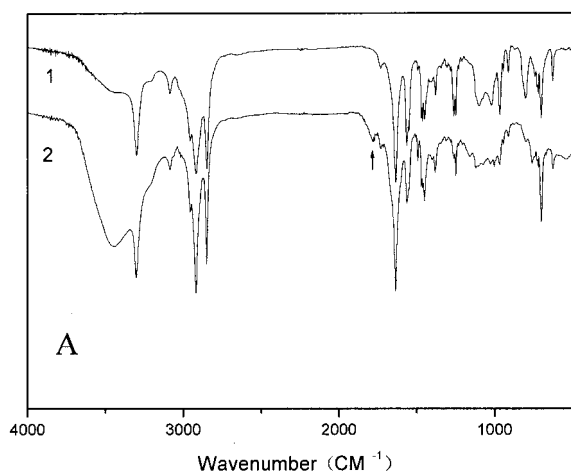


Figure 2 FTIR spectra of three fractions of (1) ABS and (2) ABS-g-MAH: (A) cyclohexane-soluble fraction, (B) acetone-insoluble fraction, and (C) cyclohexane-insoluble and acetone-soluble fraction.

ization whether the reaction was initiated by BPO or DCP.^{22,23} Figure 3 gives the GD of MAH as a function of the initiator concentration. The GD increased with an increasing initiator concentration. This might be because the number of free radicals, formed by the

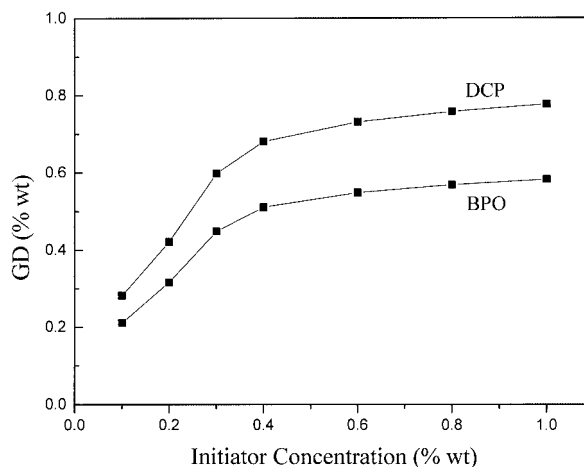


Figure 3 Effect of the initiator concentration on the GD (amount of ABS = 100 g; amount of MAH = 3.0 g; rotor speed of the twin-screw extruder = 20 rpm; temperature = 185, 190, 190, and 190°C).

decomposition of the initiator, increased, along with the grafting yield. The results also showed that DCP was a more effective initiator than BPO for the graft copolymerization reaction of MAH onto ABS at high temperatures. This was because the half-life of BPO was shorter than that of DCP at a high temperature (190°C), and BPO decay was faster and occurred before good mixing of the components. Therefore, the number of reactive sites for MAH molecules often decreased, and the free-radical further induced chain scission rather than grafting. Otherwise, a long lifetime of DCP at high temperatures was favorable for a high GD. In general, the grafting reaction was carried out in the molten state with an extruder, but the temperature of the material was low in the feed zone and high in the decompression and homogenizing zone; this gave us some inspiration to use a coinitiator (both BPO and DCP). Figure 4 presents the GD when

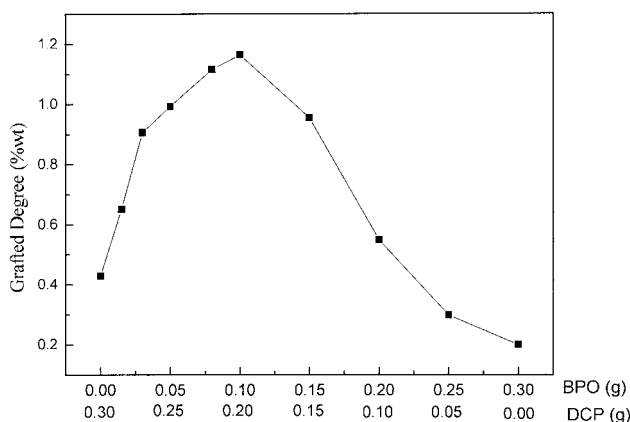


Figure 4 GD as a function of the BPO/DCP initiator composition (amount of ABS = 100 g; temperature of copolymerization = 180, 190, 190, and 190°C; rotor speed of the twin-screw extruder = 20 rpm; amount of MAH = 2.0 g).

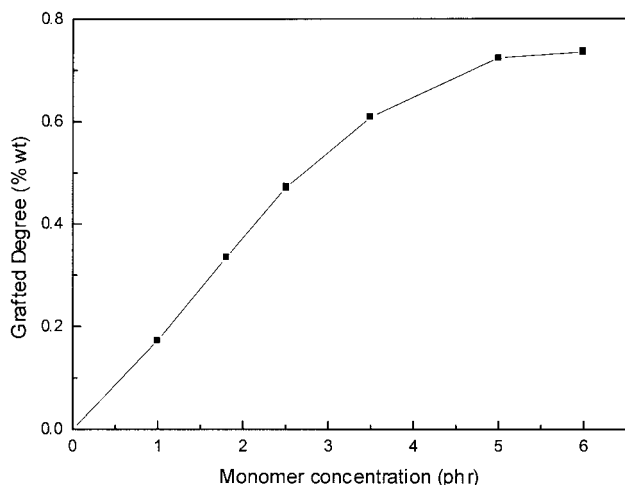


Figure 5 Effect of the monomer concentration on the GD (ABS = 100 g; DCP = 0.4 g; temperature of copolymerization = 185, 190, 190, and 190°C; rotor speed of the twin-screw extruder = 20 rpm).

BPO and DCP were used as a coinitiator (the total concentration remained 0.3 g/100 g of ABS). The GD initially increased with the BPO content. When the ratio of BPO to DCP was 1 to 2, a maximum GD was obtained. Moreover, the GD was higher for the coinitiator than for BPO or DCP. Consequently, the binary initiators gave an appropriate transient radical concentration for the copolymerization in the whole reaction zone of the extruder and, therefore, a high GD.

Effect of the MAH concentration

Figure 5 shows that the grafted degree increased with an increase in the MAH concentration. This may be because the number of monomer molecules diffusing throughout the reaction medium and reaching the polymer backbone governed the extent of grafting. The monomer acted as a trap for radicals that otherwise would have undergone chain scission or crosslinking. Therefore, a higher monomer concentration could result in less degradation of ABS. The same was observed for other grafting reactions onto ABS.^{14,16}

Effect of the comonomer

To minimize side reactions, it is important to trap radicals on the ABS backbone as rapidly as possible. Some monomers are more effective in trapping such radicals because of their relatively high solubility in the ABS melt or the inherent reactivity of the monomers.

Some studies on enhancing grafting efficiency have involved the use of mixed monomer systems; in particular, the synergistic effects of monomers may lead to more efficient grafting processes. This strategy in-

volves choosing a monomer combination in which the comonomer is effective in trapping the radicals formed on the polyolefin backbone and the resultant propagating radicals are highly reactive toward the desired monomer.²³ Furthermore, a mixture of monomers may also influence the extent of grafting of the individual monomer onto the substrate polymers, especially when synergism occurs during such a reaction.²⁴ Such grafting reactions can also give more economical grafts under the most favorable reaction conditions. As a comonomer, styrene can effectively improve the grafting reaction of MAH with a polyolefin.^{4,5} In this study, binary systems of styrene and MAH with various compositions were investigated for the grafting of MAH onto ABS (Fig. 6). The GD initially increased with increased styrene content to reach a maximum at a comonomer composition of 40/60 (w/w) St/MAH. Then, it decreased with a further increase in the styrene content. This showed that a synergistic effect in the grafting process of a styrene and MAH binary mixture onto ABS occurred, and the styrene content in the binary monomer mixture had a considerable influence on the reaction rate in the grafting process. Moreover, the extent of synergism was dependent on the relative proportions of styrene and MAH in the grafting system, and the GD for a comonomer mixture was higher than that obtained for the individual grafting of styrene or MAH (Fig. 7). In the styrene-MAH system, the improved grafting yields could be attributed to the formation of a charge-transfer complex between styrene and MAH and to the higher reactivity of this species versus that of MAH (or styrene).^{23,25}

Effect of the screw speed

Figure 8 illustrates the effect of the screw speed on the GD. The GD increased up to a certain value with

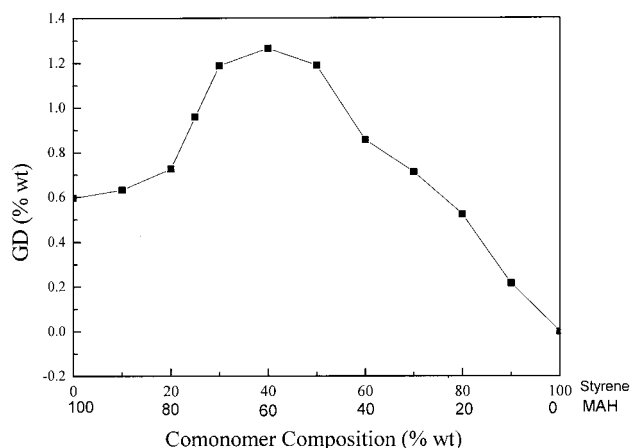


Figure 6 Effect of the styrene/MAH comonomer composition on the GD onto ABS (amount of ABS = 100 g; amount of DCP = 0.4 g; temperature of copolymerization = 185, 190, 190, and 190°C; rotor speed of the twin-screw extruder = 20 rpm).

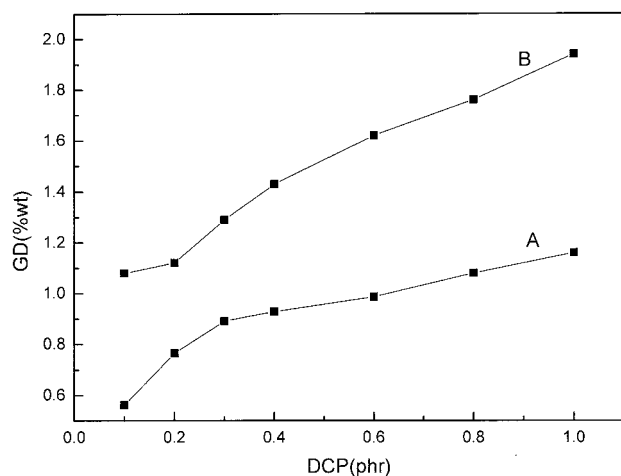


Figure 7 Effect of styrene on the grafting reaction (amount of ABS = 100 g; amount of MAH = 3.5 g; rotor speed of the twin-screw extruder = 20 rpm; temperature = 185, 190, 190, and 190°C): (A) no comonomer and (B) styrene as a comonomer (MAH/styrene ratio = 3:1).

increasing screw speed and then decreased with a further increase in the screw speed. The necessary residence time (reaction time) of the reactants in the reaction zone of the reactor and shearing action were needed. In the reaction process, the faster the screw speed was, the shorter the reaction time was, and the stronger the shearing force was. In general, a longer reaction time and a stronger shear force were beneficial for the grafting reaction. The appropriate screw speed was 20–40 rpm (the reaction time was about 5–3 min).

Effect of the reaction temperature

Figure 9 shows the effect of temperature on the GD. The GD increased with increasing temperature. This

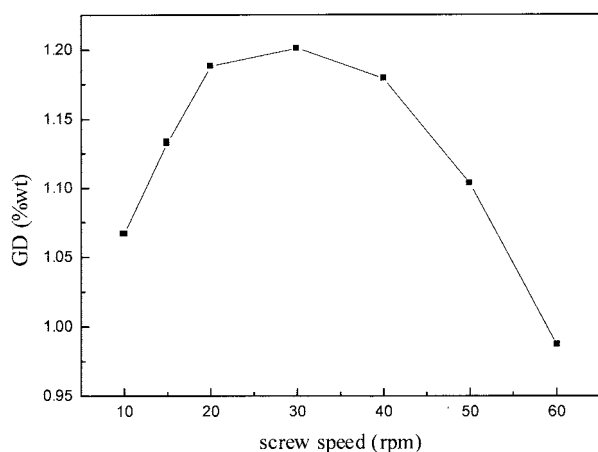


Figure 8 Effect of the screw speed on the GD (amount of ABS = 100 g; amount of MAH = 3.0 g; temperature = 185, 190, 190, and 190°C; amount of BPO = 0.1 g; amount of DCP = 0.2 g; amount of styrene = 1.0 g).

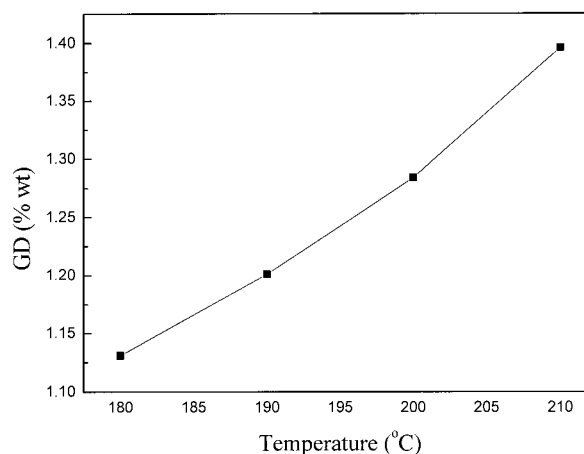


Figure 9 Effect of the molten temperature on the GD (amount of ABS = 100 g; amount of MAH = 3 g; amount of styrene = 0.75 g; amount of BPO = 0.1 g; amount of DCP = 0.2 g; screw speed = 30 rpm).

might be because the number of radicals and their mobility increased and the melt viscosity decreased at high temperatures, and this resulted in the increase in the GD.

CONCLUSIONS

MAH was successfully grafted onto ABS in the melt, and grafting occurred in the butadiene region of ABS. Using a binary initiator and a comonomer (styrene) was effective in improving the GD of the grafting reaction of MAH. The properties and phase structure of ABS-g-MAH will be reported in another article.

This work was financially supported by the National Natural Science Foundation of China (50390090). The authors would also like to acknowledge an informative discussion with Prof. Jie Yin.

References

1. Utracki, L. A. *Polymer Alloys and Blends: Thermodynamics and Rheology*; Hanser: Munich, 1989.
2. Scffaro, R.; Carianni, G.; La Mantia, F. P.; Zerroukhi, A.; Mignard, N.; Granger, R.; Arsac, A.; Guillet, J. *J Polym Sci Part A: Polym Chem* 2000, 38, 1795.
3. Ide, F.; Hasegawa, A. *J Appl Polym Sci* 1974, 18, 963.
4. Hegazy, E.-S. A.; Abd El-Rehim, H. A.; Khalifa, N. A.; Ali, A. E.-H. *Radiat Phys Chem* 1999, 55, 219.
5. Choi, S. H.; Nho, Y. C. *Radiat Phys Chem* 2000, 58, 157.
6. Petasch, W.; Räu chle, E.; Walker, M.; Elsner, P. *Surf Coat Technol* 1995, 74, 682.
7. Abdel-Razik, E. A. *J Photochem Photobiol A* 1992, 69, 121.
8. Abdel-Razik, E. A.; Ali, M. M.; Abdelaal, M. Y.; Sarhan, A. A. *Polym Plast Technol Eng* 1996, 35, 865.
9. Jiang, D. D.; Wilkie, C. A. *J Polym Sci Part A: Polym Chem* 1997, 35, 965.
10. Brydon, A.; Burnett, G. M.; Cameron, G. G. *J Polym Sci Polym Chem Ed* 1974, 12, 1011.
11. Cameron, G. G.; Qureshi, M. Y. *J Polym Sci Polym Chem Ed* 1980, 18, 3149.
12. Manaresi, P.; Passalacqua, V.; Pilati, F. *Polymer* 1975, 16, 520.

13. Pham, B. T. T.; Tonge, M. P.; Monteiro, M. J.; Gilbert, R. G. *Macromolecules* 2000, 33, 2383.
14. Chandrasiri, J. A.; Wilkie, C. A. *J Polym Sci Part A: Polym Chem* 1996, 34, 1113.
15. Huang, N. J.; Sundberg, D. C. *J Polym Sci Part A: Polym Chem* 1995, 33, 2533.
16. Rao, B. M.; Rao, P. R.; Sreenivasulu, B. *Polym Plast Technol Eng* 1999, 38, 967.
17. Deacon, C.; Wilkie, C. A. *Eur Polym J* 1996, 32, 451.
18. Höelderle, M.; Bruch, M.; Luechow, H.; Gronski, W.; Mühlhaupt, R. *J Polym Sci Part A: Polym Chem* 1998, 36, 1821.
19. Zhou, Z. F.; Huang, H.; Liu, N. C. *Eur Polym J* 2001, 37, 1967.
20. Zhou, Z. F.; Huang, H.; Liu, N. C. *J Polym Sci Part A: Polym Chem* 2001, 39, 486.
21. Gesner, B. D. *J Polym Sci Part A: Gen Pap* 1965, 3, 3825.
22. Jiang, D. D.; Wilkie, C. A. *Eur Polym J* 1998, 34, 997.
23. Moad, G. *Prog Polym Sci* 1999, 24, 81.
24. Hebeish, A.; Shalaby, S.; Bayazeid, A. *J Appl Polym Sci* 1982, 27, 197.
25. Hu, G. G.; Flat, J.-J.; Lambla, M. In *Reactive Modifiers for Polymers*; Al-Malaika, S., Ed.; Chapman & Hall: London, 1996; p 1.