

Synthesis and Characterization of Solid-Phase Graft Copolymer of Polypropylene with Styrene and Maleic Anhydride

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ABSTRACT: Polypropylene (PP) was modified by solid-phase graft copolymerization with maleic anhydride (MAH) and styrene (St), using benzoyl peroxide as the initiator and xylene as the interfacial agent. Effects of various factors such as monomer concentration, monomer ratio, initiator concentration on grafting percentage, and acid value were investigated. The graft copolymer was characterized by Fourier transform infrared, pyrolysis gas chromatography—mass spectroscopy, and dynamic mechanical analysis, and the intrinsic viscosity of the extractive from the reaction product was investigated. The results showed that the grafting percentage and acid value of the graft copolymer of PP with two monomers (MAH and St) were considerably higher than those of the graft copolymer of PP with MAH alone. The graft segments were shown to be the copolymer of St and MAH with a substantial molecular weight. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2482–2487, 2000

Key words: solid-phase grafting; polypropylene; styrene; maleic anhydride

INTRODUCTION

Polypropylene (PP) is one of the most commonly used plastics because of its good properties, wide applicability, and low cost. In recent years, there is an increasing interest in graft copolymerization of PP with maleic anhydride (MAH) or other monomers. Graft copolymerization with MAH or other polar monomers can introduce polar groups on the nonpolar PP backbone and hence overcome the disadvantage of low surface energy of PP. This not only improves the printing, coating and antistatic properties of PP surface, but also the compatibility between PP and other polar polymers, especially some engineering plastics, as

well as the adhesion between PP and fillers or fibers. Hence, it plays an important role in the development of PP based polymer alloys and composites. Similarly, grafting of some nonpolar monomers, for example styrene, onto PP has also been studied in order to improve the compatibility of PP with other nonpolar polymers.

Graft copolymerization of PP with MAH or other monomers can be performed in a solution, the melt, an aqueous suspension, or a solid state. Solid-phase graft copolymerization is a relatively new method developed in the early 1990s.^{1–4} It is performed below the melting point of PP powder, normally with a high concentration of initiator and some interfacial agent. Compared with other grafting methods, solid-phase grafting has many advantages such as lower reaction temperature, free from the need for solvent recovery and simpler equipment requirement. So far, studies on

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solid-phase graft copolymerization of PP are mainly based on one monomer, such as MAH,¹⁻⁸ unsaturated carboxylic acid,⁹ styrene,¹⁰ and methacrylic acid.¹¹ Because the self-polymerization reaction of MAH is very poor, the MAH graft segments only exist as a monomer or a short branch on the PP chains,^{7,12} and the grafting percentage is low (<5%).

In a recent study,¹³ we found that solid-phase graft copolymerization of PP with two monomers, MAH and styrene (St), significantly increased the grafting percentage and grafting efficiency. In this study, PP was solid-phase grafted with MAH and St by using benzoyl peroxide (BPO) as the initiator and xylene as the interfacial agent. The effects of various factors such as monomer concentration, monomer ratio, and initiator concentration on grafting percentage, grafting efficiency, and acid value were investigated. The structure of the graft copolymer was characterized by Fourier transform infrared (FTIR) spectroscopy, pyrolysis gas chromatography—mass spectroscopy (PyGC-MS), and dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

The polypropylene powder, provided by Guangzhou Yin Zhu Polypropylene Co., Ltd., had an isotacticity index of 98.6% and a melt flow index of 2.17. The St monomer, a chemically pure reagent, was washed with a 10% KOH solution to remove the inhibitor, then washed with distilled water and dried by molecular sieve before use. The MAH monomer, also a chemically pure reagent, was used as received without purification. BPO was chemically pure and recrystallized with alcohol before use.

Synthesis of PP-g-(MAH-St)

The graft copolymerization process was performed in a stainless steel reactor. PP, St, MAH, BPO, and xylene were mixed in a predetermined proportion and reacted in nitrogen at 120°C for 1 h. The reaction products were washed with hot ethanol and hot water, and then dried under a reduced pressure at 80°C to a constant weight.

Determination of Grafting Percentage, Grafting Efficiency, and Acid Value

Known amounts of the reaction products were extracted in a Soxhlet extractor with butanone for

16 h and then dried at 80°C until a constant weight was reached. The grafting percentage (GP) and grafting efficiency (GE) were calculated according to the following equations:

$$\text{GP}\% = \frac{W_{gp} - W_{pp}}{W_{pp}} \times 100$$

$$\text{GE}\% = \frac{W_{gp} - W_{pp}}{W_m} \times 100$$

where W_{gp} is the sample mass after extraction, W_{pp} is the mass of PP in the sample, and W_m is the mass of reacted monomers.

In order to determine the acid values of the extracted graft copolymers, they were dissolved in xylene and heated to the boiling temperature for 1 h, and then titrated by a KOH-ethanol standard solution. The phenolphthalein indicator (a solution of 1% phenolphthalein in methanol) was used. A blank titration was carried out by the same method. The acid value (AV) was determined by the following equation:

$$\text{AV}(\text{mg KOH/g}) = \frac{56.1 \times (V - V_0) \times C}{M}$$

where V is the volume (mL) of the KOH-ethanol standard solution used to titrate the sample, V_0 is the volume (mL) of the KOH-ethanol standard solution used to titrate the blank sample, C is the concentration (mol/L) of the KOH-ethanol standard solution, M is the mass (g) of the sample, and 56.1 is the molecular weight of KOH.

Fourier Transform Infrared Spectroscopy

The extracted graft copolymer powder was refined with xylene and molded into tablets with KBr powder. The FTIR spectra were determined on a Nicolet 710 FTIR Spectrometer.

Pyrolysis Gas Chromatography-Mass Spectroscopy

The pyrolysis process was carried out in a JHP-3S Curie Point Pyrolyzer (Japan Analytical Industry Co. Ltd.). The pyrolyzer was coupled to a Hewlett Packard (Model 6890) Gas Chromatography equipment. Several kinds of pyrofoils were used to determine the optimum pyrolysis temperature. The pyrolysis time was 5 s. The pyrolysis products were split in the 250°C injection port, at a split ratio of 50 : 1, and separated on a fused-silicon capillary column (HP-5, 30 m × 0.25 mm i.d.)

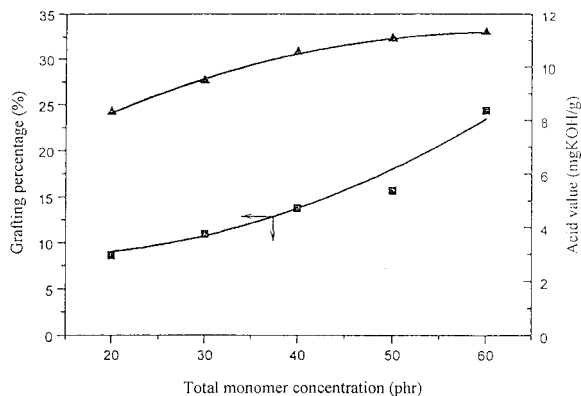


Figure 1 Effects of total monomer concentration on grafting percentage and acid value. St/MAH = 70/30; BPO = 2 phr.

using the following temperature program: maintained at 50°C for 2 min, raised to 280°C at 5°C/min, and maintained at 280°C for 5 min. The carrier gas was helium with a flow rate of 1 mL/min. The output from the GC equipment was transferred through a transfer line (280°C) to the ion source of a Hewlett Packed Mass Spectrometer (Model 5973) with an electron impact ionization voltage of 70 eV.

Dynamic Mechanical Analysis

The extracted graft copolymer powders were press molded into sheets, 1 mm thick. The analysis was carried out in a TA 2980 Dynamic Mechanical Analyzer in a single cantilever mode. The testing frequency was 1 Hz and the heating rate was 3°C/min.

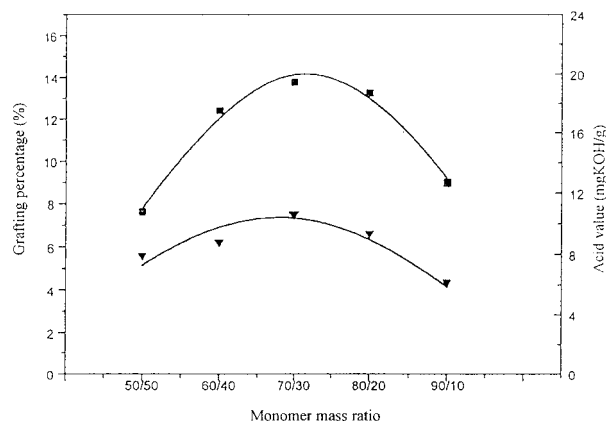


Figure 2 Effects of St/MAH ratio on grafting percentage and acid value. Total monomer concentration = 40 phr; BPO = 2 phr.

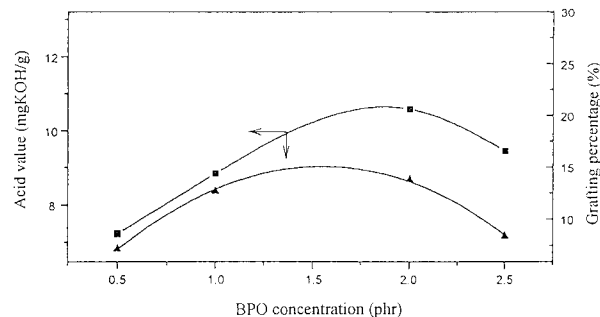


Figure 3 Effects of initiator concentration on grafting percentage and acid value. Total monomer concentration = 40 phr; St/MAH = 70/30.

RESULTS AND DISCUSSION

Effects of Total Monomer Concentration

The effects of total monomer concentration on grafting percentage and acid value are illustrated in Figure 1. Both the grafting percentage and acid value increase with increasing total monomer concentration within the studied range of 20–60 phr. At the high end of the total monomer concentration, however, the rate of increase in acid value diminishes. This may be explained by the fact that, at a low total monomer concentration, St and MAH tend to graft alternatively onto the PP backbone, causing the grafting percentage and acid value to increase at a given rate. When the total monomer concentration has reached a certain level, copolymerization between ST and MAH becomes significant. This will deplete the amount of MAH available for the grafting process, hence causing a drop in the rate of increase in acid value. Meanwhile, the remaining St monomers, because of their higher concentration than MAH, continue to graft onto the PP chains.

Effects of Monomer Ratio

Figure 2 shows the effects of monomer ratio on grafting percentage and acid value. It can be seen that both the maximum values of GP and AV appear approximately at St/MAH = 70/30. This is probably due to the fact that the ability of MAH to polymerize is low. It tends to graft either directly onto a PP chain or onto a St radical, which has already grafted on the PP chain. Since St has a higher ability to polymerize than MAH, therefore, not only can it graft directly onto a PP chain or onto a MAH graft but also onto another St radical. In other words, St stands a higher chance of grafting onto a PP chain indirectly through reaction

Table I Effects of Different Monomer Systems on Graft Copolymerization of PP^a

Sample No. ^a	Grafting System	Monomer Concentration (phr)	St/MAH Ratio	Grafting Percentage (%)	Acid Value (mg KOH/g)	Grafting Efficiency (%)
1	PP-g-(St-MAH)	40	70/30	16.9	13.1	43.5
2	PP-g-MAH	12	0/100	1.8	9.4	16.4
3	PP-g-St	28	100/0	10.2	—	39.8
4	PP-g-(St-MAH)	40	70/30	18.9	18.8	49.6
5	PP-g-MAH	12	0/100	1.5	6.6	13.9
6	PP-g-St	28	100/0	8.0	—	32.0

^a Samples 1–3 reacted in N₂; samples 4–6 reacted in air.

with either a grafted MAH or St radical. When the relative amount of styrene becomes too high, however, the trend of self-polymerization increases whereas the trend of chain transfer to PP will decrease, resulting in a drop in GP and AV.

Effects of Initiator Concentration

The effects of initiator concentration on grafting percentage and acid value are shown in Figure 3. The observed curve is typical for graft copolymerization reaction via chain transfer. The initial increases in GP and AV are caused by an increase in the concentration of initial radicals formed through reaction with the initiator, the higher the concentration of the initial radicals, the more the chain transfer to the polymer backbone. However, an excessive concentration of the initiator increases the trend of copolymerization between MAH and St, which tends to terminate the grafting reaction, as a result, GP and AV will drop.

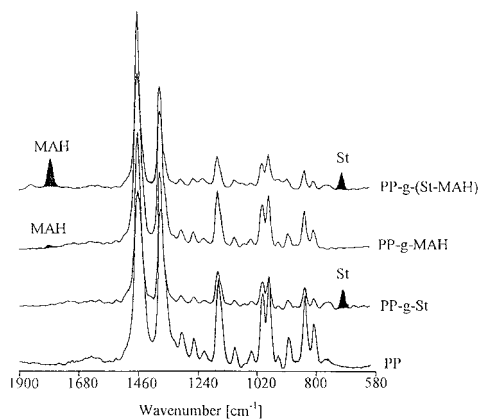


Figure 4 FTIR spectra of pure PP and PP grafted with different monomer systems; refer to samples 1–3 for details of monomer systems.

Comparison of Different Monomer Systems

The results in Table I show that the grafting percentage, grafting efficiency, and acid value of the graft copolymer containing two monomers, PP-g-(St-MAH), are far higher than those of PP-g-MAH or PP-g-St containing only one monomer. This indicates that solid-phase grafting of PP with the two monomers is advantageous for increasing the grafting percentage, grafting efficiency, and content of MAH compared with one monomer of either MAH or St.

FTIR Studies

The FTIR spectra of pure PP, PP-g-(St-MAH), PP-g-MAH, and PP-g-St are given in Figure 4.

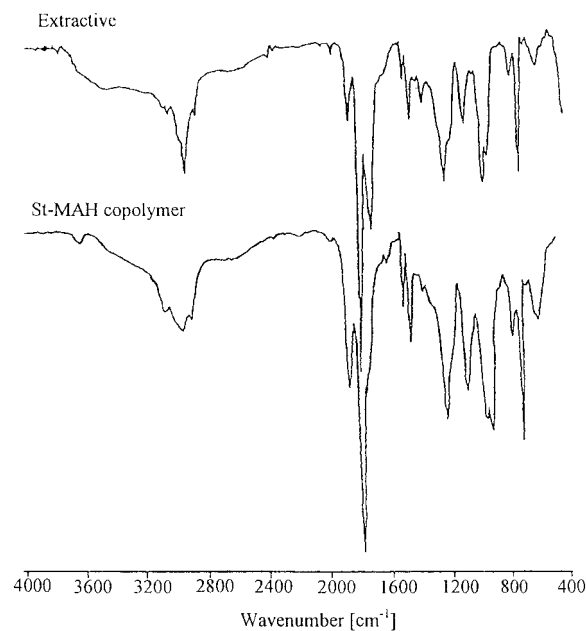


Figure 5 FTIR spectrum of the extractive from PP-g-(St-MAH) and the library spectrum of St-MAH copolymer.

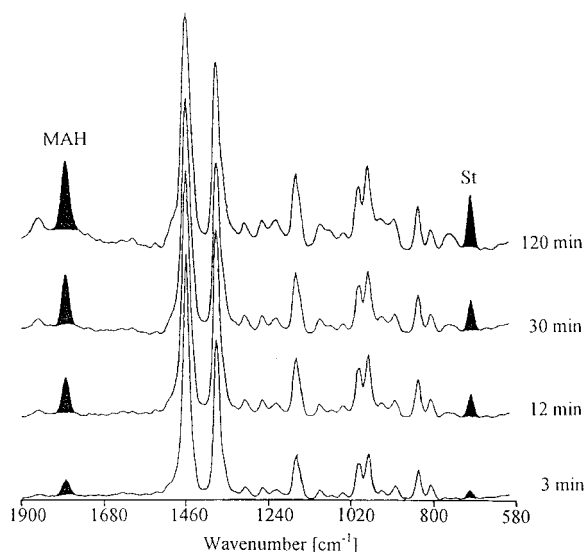


Figure 6 FTIR spectra of PP-g-(St-MAH) for different reaction times.

The absorption bands at 1789 and 706 cm^{-1} in the spectrum of PP-g-(St-MAH) are characteristic of the carbonyl group in maleic anhydride and the benzene ring in styrene, respectively. Therefore it is confirmed that both maleic anhydride and styrene are grafted onto the polypropylene backbone. Under the same grafting condition, the absorption at 1789 cm^{-1} of PP-g-(St-MAH) is far stronger than that of PP-g-MAH, indicating that solid phase grafting with the two monomers significantly increases the amount of MAH grafted onto PP. Since the ability of MAH to polymerize is

weak, the additional amount of MAH (compared with PP-g-MAH) is likely in the form of a copolymer with St. The formation of the St-MAH copolymer during the grafting process is clearly shown in Figure 5, which shows the FTIR spectrum of the extractive from PP-g-(St-MAH) and the library spectrum of St-MAH copolymer. On the other hand, there is no apparent increase in the intensity of the absorption band at 706 cm^{-1} of PP-g-(St-MAH) compared with that of PP-g-St. This suggests that the presence of MAH has little effect on the amount of St grafted on PP. The amount of St grafted onto PP is probably dependent on the availability of St radicals at the grafting sites.

Figure 6 shows the spectra of PP-g-(St-MAH) for different lengths of reaction time. It can be seen that the intensities of the characteristic bands of St and MAH gradually increase with increasing reaction time and the intensities of the bands for any given time are approximately proportional. This again provides a strong hint that the two monomers combine a given ratio to form a copolymer.

PyGC-MS Characterization

The characterization of PP-g-(St-MAH) by PyGC-MS has seldom been reported. In order to determine the optimum pyrolysis temperature, a series of experiments, 255, 423, 486, and 590 $^{\circ}\text{C}$, by using several kinds of pyrofoils, were conducted. At last, it was found that pyrolysis at 423 $^{\circ}\text{C}$ was optimum for PP-g-(St-MAH). Figure 7 shows the

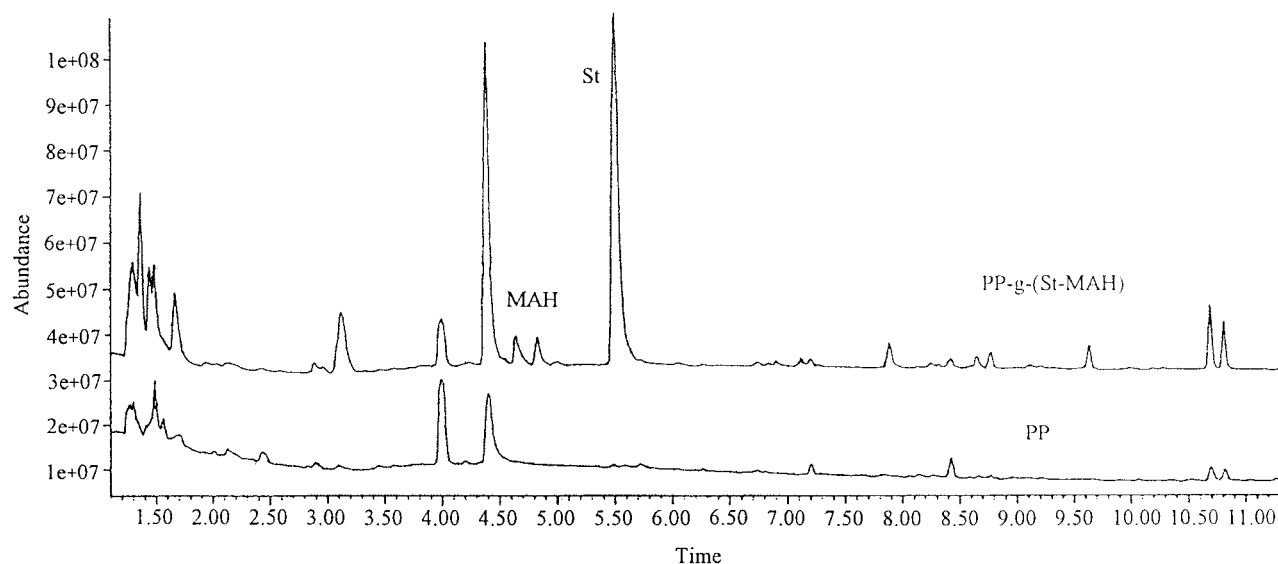


Figure 7 Overlay of pyrograms of PP and PP-g-(St-MAH) for 0–11 min.

overlay of the pyrograms of PP and PP-g-(St-MAH) for time $t = 0$ –11 min. The characteristic peaks of MAH and St can be determined at $t = 4.66$ and 5.51 min, respectively, by using the mass spectrometer. It is another proof that maleic anhydride and styrene were grafted onto the PP backbone.

DMA and Intrinsic Viscosity Measurement

Figure 8 shows the DMA results of the pure PP and PP-g-(St-MAH). It can be seen that the pure PP has only one T_g but PP-g-(St-MAH) has two: the first T_g (14.9°C) is of the PP backbone, and the second (104.4°C) is likely caused by the relaxation of the grafted St-MAH segments. In other words, the grafted St-MAH copolymer segments have a substantial molecular weight.

In order to confirm that the graft copolymer PP-g-(St-MAH) has long side chains with a substantial molecular weight, the intrinsic viscosities $[\eta]$ of the extractives from the reaction products with different total monomer concentrations were determined (Fig. 9). It is apparent that the intrinsic viscosities $[\eta]$ of the extractive solutions, or the molecular weights of the extractives, increase with increasing total monomer concentration, suggesting an increase in the molecular weight of the grafted side chains.

CONCLUSIONS

Maleic anhydride and styrene can be grafted onto the isotactic polypropylene powder in a solid

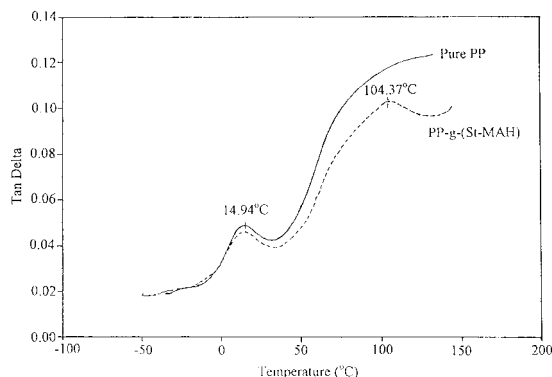


Figure 8 DMA results of pure PP and PP-g-(St-MAH).

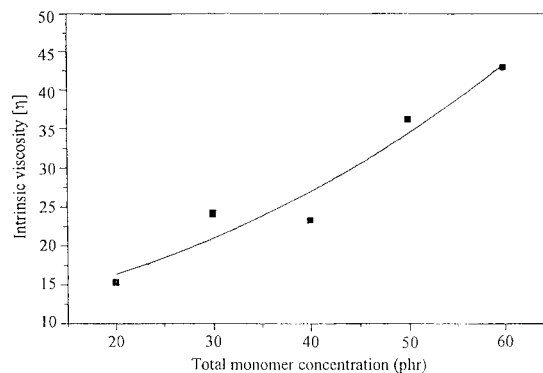


Figure 9 Relation between intrinsic viscosity of extractive from PP-g-(St-MAH) and total monomer concentration.

phase. The grafting percentage and acid value of PP-g-(St-MAH) are affected by the total monomer concentration, monomer ratio, and initiator concentration, and are considerably higher than those of PP-g-MAH. The grafted segments are shown to be the copolymer of St and MAH with a substantial molecular weight.

REFERENCES

- Rengarajan, R.; Vivic, M.; Lee, S. *Polymer* 1989, 30, 933.
- Rengarajan, R.; Vivic, M.; Lee, S. *J Appl Polym Sci* 1990, 39, 1783.
- Lee, S.; Rengarajan, R.; Parameswaran, V. R. *J Appl Polym Sci* 1990, 41, 1891.
- Rengarajan, R.; et al. *Eur Polym J* 1990, 31, 1703.
- Khunova, V.; Zamorsky, Z. *Polym Plast Technol Eng* 1993, 32, 289.
- Borsig, E.; Hreckova, L. *Pure Appl Chem* 1994, A31, 1447.
- Tong, S.; Xie, X.; Zhang, L. *Synthetic Resin and Plastics* 1994, 11, 15 (in Chinese).
- Yang, M. *China Plast Ind* 1995, 2, 6 (in Chinese).
- Enikolopov, N. S.; Sizova, M. D.; Bunina L. O.; et al. *Vysokomolekularnye Soedineniya, Seriya A*, 1994, 36, 608 (in Russian).
- Li, Q.; Li, C.; Rui, Z.; et al. *Mod Plast Process Appl* 1996, 8(1), 14 (in Chinese).
- Lin, Z.; Yan, W.; et al. *China Plastics Industry* 1996, 6, 67.
- Russell, K. E.; Kelusky, E. C. *J Polym Chem* 1998, 26, 2273.
- Jia, D.; Luo, Y.; Li, Y.; Lu, H.; Fu, W.; Cheung, W. L. *Second East Asian Polymer Conference, Hong Kong, January 12–16, 1999*, 369.