BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 6, pp. 1269–1273, 1995

0032-3861/95/$10.00+0.00

Synthesis of PBA/PMSAN core–shell graft copolymer and its application as a processing aid for PVC

Jungang Gao*, Zhiting Li, Zengqi Shan and Zihua Yao
Department of Chemistry, Hebei University, Hebei Province, Baoding 071002, People's Republic of China
(Received 27 December 1993; revised 25 April 1994)

The core–shell graft copolymer of α-methyl styrene with acrylonitrile on poly(butyl acrylate) was synthesized. The graft polymerization was investigated as a function of reaction temperature, initiator concentration used in the secondary polymerization, monomer to polymer ratio and emulsifier concentration. The compatibility of this core–shell graft copolymer with poly(vinyl chloride) (PVC) was determined by the solubility parameter method and scanning electron microscopy. The mechanical and rheological behaviour of the blend show that this core–shell graft copolymer can be used as a processing aid for PVC.

(Keywords: graft copolymer; synthesis; poly(vinyl chloride))

INTRODUCTION

The modification of poly(vinyl chloride) (PVC) by adding another polymer is a method currently used in practice. The number of polymers and copolymers applied as modifiers is quite large and may be divided into two basic groups. The first group involves rubber-like polymers and copolymers which are added to PVC to improve its mechanical properties, in particular its toughness. The other group of modifiers involves polymers which are used for the modification of PVC under the general denomination of processing aids. When the processing aids are added to PVC, the processing melt viscosity is lowered and processing operations (such as milling, calendering, extrusion and blow moulding) in melts are significantly facilitated. The mechanical properties of hard PVC are changed only insignificantly at room temperature by the addition of a processing aid.

The impact resistance aid usually used for hard PVC is poly(butyl acrylate)–poly(methyl methacrylate) (PBA/PMMA) core–shell graft copolymer. The processing aids usually used are PMMA and its copolymer[1–3]. The oligomer of poly(α-methyl styrene) (PMS) was used as a processing aid for resins[4], but the copolymer of α-methyl styrene (MS) with acrylonitrile (AN) (PMSAN) has not been used as a processing aid for PVC. Many core–shell copolymers have been synthesized and investigated[5,6], but the core–shell copolymer of PBA/PMSAN has not been synthesized or used as a processing aid for PVC to date.

The object of this paper is to describe the synthesis of the PBA/PMSAN core–shell graft copolymer latex and to investigate its use as a processing aid for PVC. The compatibility of the PBA/PMSAN copolymer with PVC, and its rheological behaviour and the mechanical properties of mixtures of PBA/PMSAN copolymer with PVC are investigated.

EXPERIMENTAL

Materials

The monomers, n-butyl acrylate (BA), acrylonitrile (AN) and divinylbenzene (DVB) were washed with aqueous sodium hydroxide to remove the inhibitor. The BA, AN and MS were freshly distilled. Sodium dodecylsulfate (SDS) was used as emulsifier. Potassium persulfate ($K_2S_2O_8$) was used as initiator. Solvents used to determine the solubility parameter of PMSAN were all analytically pure grades. Distilled deionized water (DIW) was used in all polymerizations. The chain transfer agent, tertiary dodecylmercaptan (TDM), was used as received. PVC, tribasic lead sulfate (TLS), dibasic lead phosphite (DLP), barium stearate (BS) and wax were all commercial grade.

Core–shell emulsion polymerization

The BA seed latex particles were synthesized by emulsion polymerization and all components were purged under N_2 for 10 min. The SDS and DIW were charged to a four-necked glass flask, followed by part of the BA/DVB mixture. The reaction vessel was then heated to 80°C and the mixture was stirred. The $K_2S_2O_8$ solution was added. After 15 min the remainder of the BA/DVB mixture was added over the course of 1.5 h under nitrogen atmosphere. The reaction was then held at 85°C for an additional 2 h. The sample was purified with warm DIW and dried. The conversion was measured gravimetrically.

Two-stage latex polymers were prepared by charging

---

* To whom correspondence should be addressed

the prepurged seed latex to a four-necked glass flask. The mixture of MS, AN and $K_2S_2O_8$ was added dropwise over 1.5 h. The reaction was held at 70°C for an additional 3 h. The Na_3PO_4 solution was used to maintain the pH of the reaction system at 6–7. After the reaction, the $Al_2(SO_4)_3$ solution was added to precipitate the copolymer. The copolymer was washed with warm DIW then dried *in vacuo.*

The overall percentage conversion was measured gravimetrically and the MS percentage conversion was determined by the bromination method[7].

Determination of the degree of grafting

The degree of grafting was determined by the method of extraction[8]. The dried core–shell polymer samples were put into a Soxhlet extractor; cyclohexane was used as the volatile extraction solvent. The ungrafted PBA was dissolved and isolated from the core–shell copolymer. The degree of grafting was calculated using mass balance.

Determination of solubility parameter

The copolymer PMSAN with the same composition as the shell was synthesized by emulsion polymerization. This copolymer was dried *in vacuo* at 50°C, and then dissolved in acetone. The turbidity of this solution was determined by the method of titration with a precipitating agent.

Electron microscopy

The morphology and particle size of the core–shell latex particles were determined by transmission electron microscopy[5]. The morphology of the mixture of core–shell copolymer with PVC was studied by scanning electron microscopy using the method of Zelinger[2]. The same sample was put in acetone for 8 h and was then analysed by scanning electron microscopy. The compatibility of PBA/PMSAN copolymer with PVC was investigated.

Preparation of samples

PVC was mixed with a determined quantity (weight percentage) of processing aid and a lubricant and a stabilizer were added to this mixture; the recipes are given in *Table 1*. All components were first mixed in a mixer and then milled on a laboratory two-roll mill at 155–175°C for 10 min. Plates 2 mm thick were pressed at temperatures of 170–190°C. After cooling in a cooling press the plates were tempered for a period of 12 h at 90°C. Dumbbell-shaped samples for tensile tests were cut from the plates. The samples for notch impact tests and hardness tests were all 120 mm x 15 mm x 5 mm.

Determination of rheological behaviour

The rheological behaviour of mixtures of PBA/PMSMA copolymer with PVC was investigated by a Shimadzu Koka Flow Tester[9,10]. The fixed temperature method was used. The nozzle diameter was 1 mm and the nozzle length was 2.38 mm. The weight of the test specimen was 1.5 g.

Table 1 Recipes of components of experimental specimens

Specimen	0	1	2	3	4	5
PVC(w)	100	100	100	100	100	100
TLS	3	3	3	3	3	3
DLP	2	2	2	2	2	2
WAS	0.2	0.2	0.2	0.2	0.2	0.2
BS	2	2	2	2	2	2
PBA/PMSAN	0	4	6	8	10	12

Determination of mechanical properties

Tensile testing was performed using an electronic tensile tester. Tests were conducted at an extension rate of 12.0 mm min^{-1} at 25°C and 50% relative humidity. The notch impact tests and hardness tests were carried out on a XCJ-40 impact tester and a Brinell hardness tester, respectively.

RESULTS AND DISCUSSION

Effect of emulsion polymerization on grafting reaction

The grafting reaction was the primary concern in this study. In the PBA/PMSAN core–shell emulsion polymerization, the grafting reaction can occur through reaction of the residual double bond in PBA or by a hydrogen abstraction mechanism in the allyl position. All of the grafting possibilities involve combinations of reactive groups, compositions of the PBA and free radical species and some other reaction. The effects of emulsion polymerization parameters on the graft reaction are discussed.

With neither the concentrations of initiator and emulsifier nor the core–shell ratio being taken into account (in the same recipe), the emulsion polymerization was carried out at different temperatures. In these reactions the percentages of core PBA grafted by the copolymer PMSAN are shown to increase with rise in temperature to a maximum of about 75°C. After 75°C the amount of PBA grafted by PMSAN decreases with rise in temperature. A possible explanation is that the initiator was activated when the temperature was raised, but the rate of PMSAN copolymer coupling termination is increased at higher temperature.

When the concentration of initiator was constant, and the core–shell ratio and temperature were constant at 1:1.2 and 75°C, respectively, a series of experiments was carried out at various specific surface areas of seed latex or at different emulsifier concentrations for PBA seed latex. As shown in *Figure 1*, the percentage of PBA grafted by PMSAN increases linearly with increasing specific surface area of the seed latex. The results indicate that the grafting reaction is dependent on surface area, the site of initiation being in either the aqueous phase or the adsorbed emulsifier layer[5].

Figure 2 shows the percentage of PBA grafted when the reactions were carried out at different shell–core ratio. From the data presented in *Figure 2*, it is obvious that the amount of PBA grafted by PMSAN increased as the shell–core ratio increased, at lower shell–core ratios. However, at higher shell–core ratios the amount of PMSAN grafted onto core PBA decreased with increasing shell–core ratio. In order to explain the reduced levels of PMSAN grafted onto PBA as a function of increasing shell–core ratio, recall the experiment in which grafting was investigated as a function of seed surface area. From these studies, it was concluded that grafting is a surface-controlled process. This process involves initiation either in the aqueous phase or, more likely, in the adsorbed emulsifier layer, followed by capture of the growing radicals by existing monomer-swollen particles. As

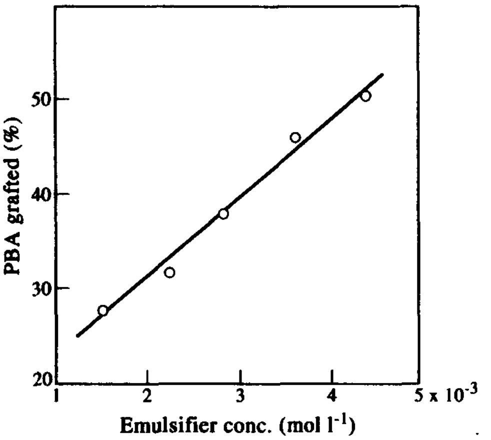

Figure 1 Percentage PBA grafted *versus* concentration of emulsifier in a 40/60 PBA/PMSAN core–shell latex

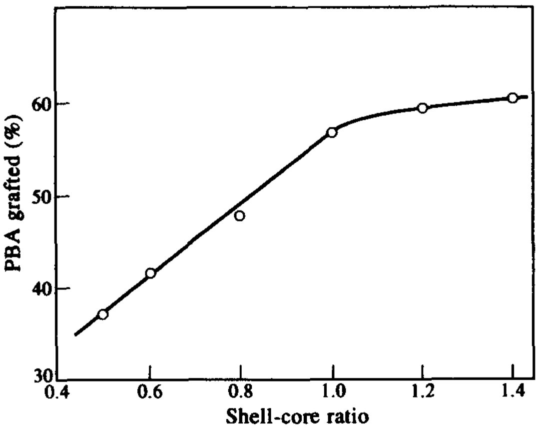

Figure 2 Percentage PBA grafted by PMSAN *versus* shell–core ratio for the PBA/PMSAN core–shell emulsion polymerization

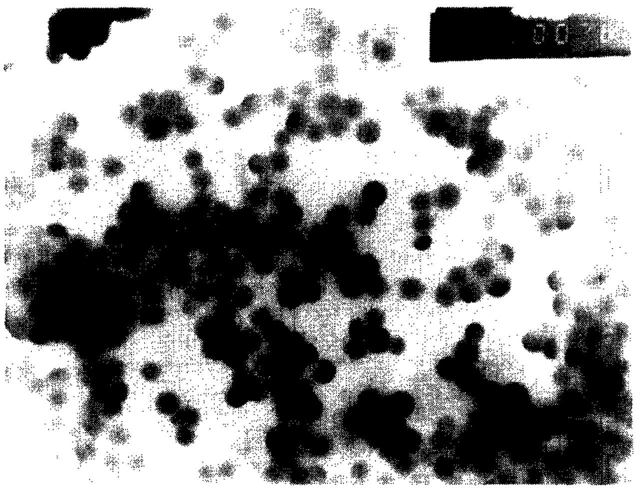

Figure 3 Transmission electron micrographs for 40/60 PBA/PMSAN core–shell latex (magnification 25 000 ×)

grafting proceeds and a certain shell thickness of the second stage polymer is reached, the grafting reaction becomes less probable due to the reduced availability of core PBA. The morphology of the core–shell copolymer (PBA/PMSAN) is shown in *Figure 3*. From *Figure 3* the particles of the core–shell copolymer latex are seen to have a spherical geometry, with a diameter of 100–140 nm.

Compatibility of PMSAN copolymer with PVC and morphology of mixture

The compatibility of PBA/PMSAN copolymer with PVC can be estimated by determination of the solubility parameter. In order to find the compatibility of shell PMSAN with PVC, the solubility parameter of PMSAN was determined by the method of turbidity titration[10]. The sample was dissolved in acetone ($\delta_s = 20.4$), then titrated by a precipitating agent. The solubility parameter δ_{sm} of mixed solvent was calculated as follows:

$$\delta_{sm} = \Phi_1 \delta_1 + \Phi_2 \delta_2 \qquad (1)$$

where Φ_1, Φ_2 and δ_1, δ_2 are the volume fraction and solubility parameter of solvent 1 and 2, respectively. If the water ($\delta_s = 47.7$), methanol ($\delta_s = 29.6$), cyclohexane ($\delta_s = 16.7$) and hexane ($\delta_s = 14.9$) were used as precipitating agents, the solubility parameter of PMSAN copolymer may be calculated as follows:

$$\delta_p = \frac{1}{2n}(\delta_{smh_1} + \delta_{smh_2} + \cdots + \delta_{sml_n} + \delta_{sml_n}) \qquad (2)$$

From the turbidity titration experiment we determined the solubility parameter δ_p of PMSAN copolymer to be $20.54\,J^{1/2}\,cm^{-3/2}$. The solubility parameter δ_p can be calculated from the molar attraction constant F_{pi} and molar volume V_{pi} of the constitutive group[10]:

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{\sum V_{pi}} \qquad (3)$$

From equation (3), $\delta_p = 20.92\,J^{1/2}\,cm^{-3/2}$. This δ_p value is approximately equal to the solubility parameter for PVC, $19.2\text{–}22\,J^{1/2}\,cm^{-3/2}$, therefore, PMSAN is compatible with PVC.

The morphology of the mixture of PBA/PMSAN with PVC is shown in *Figure 4*. As is seen from *Figure 4*, the compatibility of PVC with PBA/PMSAN is good. Although the particles of dried PBA/PMSAN copolymer are usually larger than 1 mm diameter, the morphology of the mixture of PBA/PMSAN with PVC is uniform. Although the PBA/PMSAN copolymer can be dissolved in acetone, holes did not appear on the surface of the mixture samples after they were placed in acetone for 8 h. The samples of mixture and PVC were all swelled by acetone, and the original plane shapes disappeared.

Rheological behaviour of the mixture of PBA/PMSAN with PVC

The experimental specimens were made using the recipes shown in *Table 1*. The experimental temperature was fixed at 180°C, with experimental loads of 80, 95, 100 and 130 kg, respectively. The apparent shear stress τ_w, apparent shear rate $\dot{r}_w$ and apparent viscosity η_a were calculated using the following equations. Effective shear stress at wall of nozzle:

$$\tau_w = \frac{Pr}{2L} \qquad (4)$$

where P is applied pressure ($kg\,cm^{-2}$), r is nozzle radius (cm) and L is nozzle length (cm).

The efflux rate is given by:

$$Q = \frac{hs}{t}(cm^3\,s^{-1}) \qquad (5)$$

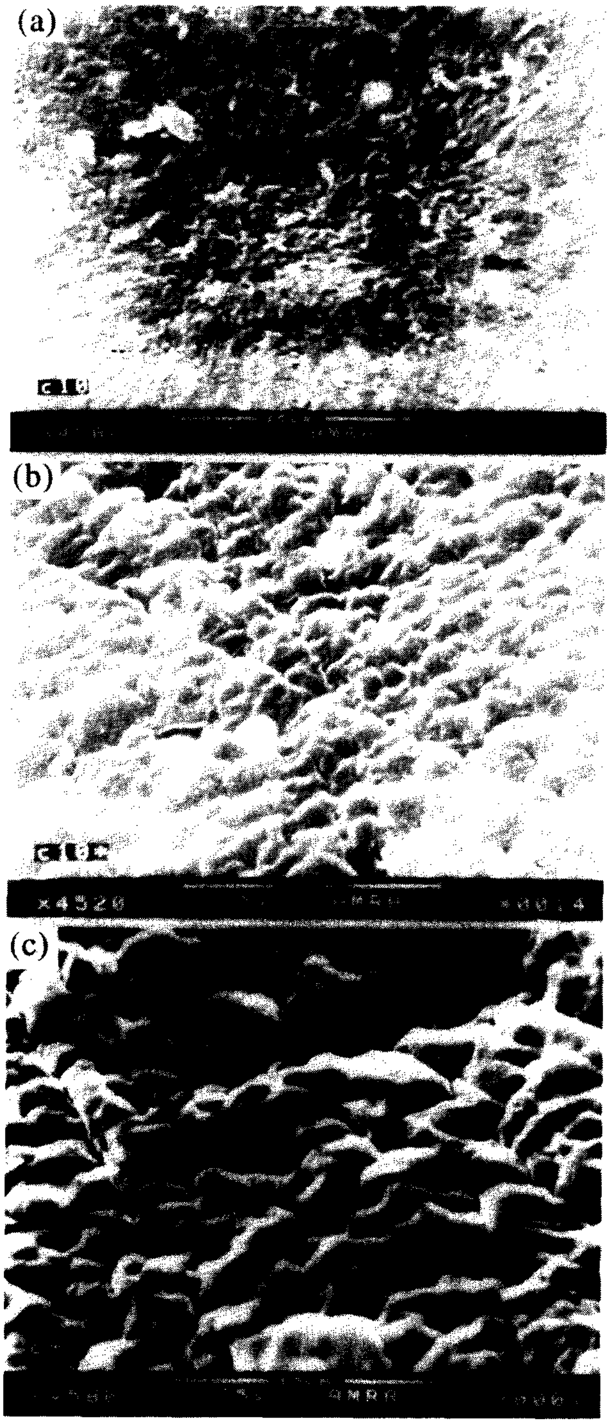

Figure 4 Scanning electron micrographs of a mixture of PBA/PMSAN copolymer with PVC (10:100). (a) Mixture of PBA/PMSAN copolymer with PVC; (b) mixture sample after 8 h in acetone; (c) hard PVC sample after 8 h in acetone

where h is downward displacement of plunger (cm), s is area of plunger (cm^2) and t is effluent time of melt (s).

The apparent shear rate at the wall of the nozzle is calculated by:

$$\dot{r}_w = \frac{4Q}{\pi r^3} (s^{-1}) \tag{6}$$

The apparent viscosity is given by:

$$\eta_a = \frac{\tau_w}{\dot{r}_w} \times 9.8 \times 10^5 \text{ (poise)} \tag{7}$$

A plot of $\log \eta_a$ *versus* $\log \dot{r}_w$ is given in *Figure 5*. As seen from *Figure 5*, the apparent viscosity η_a decreased with increasing shear rate. It is shown that the flow behaviour of this mixture in the melt is the behaviour of a pseudoplastic liquid.

Under the same conditions, the experiment was carried out at 160, 170, 180 and 190°C. According to the Arrhenius equation $\eta_a = A e^{-E/RT}$, $\ln \eta_a$ was plotted against $1/T$, and we obtained the flow activation energy E_0 and E_3 (specimen 3 in *Table 1*) as 58.20 kJ mol^{-1} and 45.45 kJ mol^{-1}, respectively. As seen from these data, the flow activation energy of the mixture melt is lower than that of PVC.

Therefore, when the PBA/PMSAN copolymer was used as a processing aid for PVC, the melt viscosity fell and decreased with increasing amount of PBA/PMSAN used. That is to say, if this copolymer were used as a processing aid for PVC, the processing teemperature for hard PVC could be lowered.

Mechanical properties

The notch impact strengths of these specimens for mixing different amounts of PBA/PMSAN are shown in *Figure 6*. As seen from *Figure 6*, the impact strength increases with increasing amount of PBA/PMSAN. Therefore, PBA/PMSAN not only lowers the processing temperature and η_a, but it can also increase the impact strength of hard PVC. In contrast the usual commercial impact-resistance processing aid, ACR, increases the

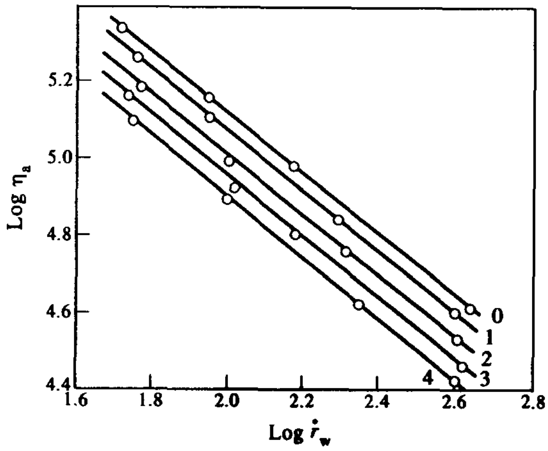

Figure 5 Apparent viscosity η_a of the mixture melt *versus* shear rate for the mixture of PBA/PMSAN copolymer with PVC at 180°C. The numbers 0–4 correspond to the specimens in *Table 1*

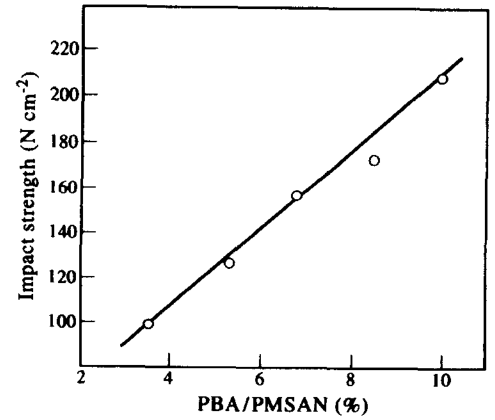

Figure 6 Relationship of impact strength and the ratio of PBA/PMSAN copolymer to PVC

Table 2 Tensile strength and hardness of improved PVC

Specimen[a]	0	1	2	3	4	5
Tensile strength ($\mathrm{N\,cm^{-2}}$)	3912	3871	3820	3760	3752	3748
Hardness ($\mathrm{kg\,mm^{-2}}$)	25.5	23.4	23.7	23.2	22.2	21.7

[a] The recipes for these specimens are similar to those given in *Table 1*

impact strength of hard PVC, but also increases the processing viscosity η_a[8]. Also, the usual processing aid cannot increase the impact strength of hard PVC[2].

The PBA/PMSAN has a lower glass transition temperature, and is a pliable component in this system. The shell of PMSAN has a good compatibility with PVC. When this material is subjected to impact, the PBA/PMSAN particles become a centre of stress, crazes or shear bands and absorb significant amounts of energy in this region. On the other hand, these pliant particles can confine the development of crazes and prevent breakage of materials[8,11].

The tensile strength and hardness of PVC improved by PBA/PMSAN are shown in *Table 2*. As seen from *Table 2*, the tensile strength and hardness decrease with increasing amount of PBA/PMSAN. This result is similar to that obtained using the general commercial processing aid and impact resistance aid ACR[2,8].

CONCLUSIONS

In the core–shell emulsion polymerization of MS–AN on PBA, the amount of grafting is controlled by the reaction temperature, initiator concentration, emulsifier concentration and core–shell ratio. The possibility of grafting increases with temperature increase to 75°C. The percentage of grafting increases with increasing emulsion surface area; it is controlled by the specific area of the emulsion particle.

The MS–AN copolymer and core–shell PBA/PMSAN copolymer have a good compatibility with PVC, and, their solubility parameters are close to that of PVC.

The PBA/PMSAN copolymer can be used as a processing aid for hard PVC, which can decrease the processing temperature and melt flow viscosity of hard PVC, but also can increase its impact strength.

When PBA/PMSAN copolymer was mixed with PVC, the tensile strength and hardness decreased. The amount of PBA/PMSAN copolymer added was 6–8%.

REFERENCES

1 Ryan, C. F. *Soc. Plast. Eng. J.* 1968, **24**, 89
2 Zelinger, J. *J. Polym. Mater.* 1976, **5**, 99
3 Reiff, G. *Kunststoffe* 1968, **58**, 277
4 Qi, Z. *China Plastics* 1992, **6**, 26
5 Merkel, M. P. and Dimonie, V. L. *J. Polym. Sci., Polym. Chem. Edn* 1987, **25**, 1755
6 Min, T. I., Klein, A., El-Aasser, M. S. and Vanderholf, J. W. *J. Polym. Sci., Polym. Chem. Edn* 1983, **21** 2845
7 Chavles, F. and Wilcox, J. 'Experimental Organic Chemistry—Theory and Practice', Macmillan Publishing Company, New York, 1984, p. 79
8 Lu, M. J. and Wu, S. H. *Plastic Technol.* 1989, **1**, 7
9 Arai, T. 'A Guide to the Testing of Rheological Properties with Koka Flow Tester', Maruzen Co. Ltd, Tokyo, 1958, p. 16
10 Cheng, Z. 'Physical Experiments in Polymer Science', Beijing University Publishing Company, Beijing, 1983, p. 196
11 Clas, S. D. and Elsenbekg, A. *J. Polym. Sci.* 1984, **22**, 1529