ELSEVIER

S0032-3861(96)00609-X

Polymer Vol. 38 No. 5, pp. 1139–1143, 1997

0032-3861/97/$17.00 + 0.00

Study on poly(butyl acrylate)/poly(α-methyl styrene-*co*-acrylate) core–shell particles as a processing aid for poly(vinyl chloride)

Juangang Gao*, Liting Yang, Kuilin Deng and Zihua Yao
Department of Chemistry, Hebei University, Hebei, Baoding, People's Republic of China
(Received 26 October 1995; revised 27 May 1996)

The core–shell graft copolyermization of α-methyl styrene-*co*-ethyl acrylate and α-methyl styrene-*co*-methyl acrylate on poly(butyl acrylate) was carried out. The compatibility of these copolymers with poly(vinyl chloride) was estimated by the solubility parameter method and scanning electron microscopy. The rheological behaviour was investigated by a flow tester. The mechanical properties, rheological behaviour and morphology of these blends show that these copolymers can be used as a processing aid for poly(vinyl chloride). © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: copolymer; rheological; morphology)

INTRODUCTION

The modification of hard poly(vinyl chloride) (PVC) by adding another polymer is a well known method currently in practice. The number of polymers and copolymers applied as PVC modifiers is quite large. Acrylic polymers can be used as PVC modifiers. The 'acrylic modifiers' comprise homo- and co-polymers of various esters of acrylic and methacrylic acids, graft copolymers of methyl methacrylate, styrene and vinyl chloride on acrylic elastomers[1–3]. These modifiers may be divided into two categories. The first one is an impact modifier which is added to PVC to improve mechanical properties, particularly toughness. The other group is the processing aid, which is used to reduce melt viscosity and to provide processing condition for milling, calendering and extrusion blow moulding.

A typical impact modifier for hard PVC is poly(butyl acrylate)–poly(methyl methacrylate) (PBA/PMMA) core–shell graft copolymer. The conventional processing aids are PMMA and a copolymer of methyl methacrylate with ethyl acrylate. The oligomer of poly(α-methyl styrene) (PMS) was also used as a processing aid for resins[4]. However, the copolymers of α-methylstyrene (MS)–methyl acrylate (MA) and MS–ethyl acrylate (EA) have not been used as a processing aid. The MS is cheaper than acrylate.

The purpose of this paper is to investigate the use of core–shell graft copolymers of PBA/poly(α-methyl styrene-*co*-methyl acrylate) (PBA/PMSMA) and PBA/poly(α-methyl styrene-*co*-ethyl acrylate) (PBA/PMSEA) as processing aids for PVC. The miscibility of PBA/PMSMA and PBA/PMSEA with PVC is discussed. The rheological behaviour, morphology and mechanical properties of the blends are investigated.

EXPERIMENTAL

Materials

The monomers, butyl acrylate (BA), methyl acrylate (MA), ethyl acrylate (EA) and divinyl benzene (DVB) were washed with aqueous sodium hydroxide to remove the inhibitor. The BA, MA and α-methyl styrene (α-MS) were freshly distilled. Sodium dodecyl sulfate (SDS) was used as emulsifier, and potassium persulfate ($K_2S_2O_8$) as initiator. All monomers, SDS and $K_2S_2O_8$ were supplied by Beijing Chemical Reagent Co. The solvents used to determine the solubility parameter of copolymers of α-MS and acrylate, and $Al_2(SO_4)_3 \cdot 18H_2O$ and Na_3PO_4, were all analytically pure grade. Distilled deionized water (DIW) was used in all polymerizations. The chain transfer agent, tertiary dodecylmercaptan (TDM), was used as received. PVC (Yanshan Chemical Co.), tribasic lead sulfate (TLS), dibasic lead phosphite (DLP), barium stearate (BS) and wax were all commercial grades, supplied by Tianjin Chemical Co.

Core/shell emulsion polymerization

The BA seed latex particles were prepared as follows: all components were purged under N_2 for 10 min. The SDS and DIW were charged to a four-necked glass flask (1 l), followed by part of a 125 g 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 remaining BA/DVB mixture was added gradually for 1.5 h under N_2 atmosphere. The reaction was then kept at 85°C for an additional 2 h.

Core–shell graft copolymers were prepared by charging the prepurged 520 g seed latex to a four-necked glass flask and by adding a mixture of 70 g α-MS, 65 g EA and 0.6 g $K_2S_2O_8$ dropwise over 1.5 h; the reaction was kept at 80°C for an additional 3 h. The Na_3PO_4 solution was used to control the pH of the reaction system between 6 and 7. After the polymerization reaction, an $Al_2(SO_4)_3$

---

* To whom correspondence should be addressed

solution was added to precipitate the copolymer latex. The products were purified by washing with warm DIW and then dried *in vacuo*. The overall percentage conversion was measured gravimetrically (it was usually 93–95%).

The PBA/PMSMA core–shell graft copolymer was synthesized in the same way.

Determination of solubility parameter

Neat shell copolymers (PMSEA and PMSMA) were synthesized by emulsion polymerization. These copolymers were dried *in vacuo* at 50°C. The samples were dissolved in acetone. The turbidity was determined by the method of titration with precipitating agent. The solubility parameter was calculated by the method of ref. 5.

Electron microscopy. The morphology of polymer mixtures of PVC with PBA/PMSMA and PBA/PMSEA copolymers was observed by scanning electron microscopy (SEM) using the method of Zelinger[2]. The sample was also placed in acetone for 8 h and then analysed by SEM.

Preparation of samples

PVC was mixed with a determined quantity of processing aid (in wt%), a lubricant (BS) and a stabilizer (TLS or DLP). All components were first mixed in a mixer at room temperature and then milled on a laboratory two-roll mill at temperatures of 155–175°C for 10 min. Two-millimetre thick plates 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 $120 \times 15 \times 5\,\mathrm{mm}^3$.

Rheological behaviour

The rheological behaviour of mixtures of PBA/PMSMA and PBA/PMSEA copolymers with PVC was investigated by a Shimadzu Koka Flow Tester[6,7]. 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.

Mechanical properties

The tensile test was performed using an electronic tensile tester. The test portion of the dumbbell specimen was 25 mm long with a cross-section $2 \times 7\,\mathrm{mm}^2$. Tests were conducted at an extension rate of $12.0\,\mathrm{mm\,min}^{-1}$ at 25°C and 50% relative humidity. The notch impact and hardness tests were carried out on an XCJ-40 impact tester and a Brinell hardness tester, respectively.

Dynamic mechanical measurements were carried out by torsional braid analysis over the temperature range −65 to 140°C.

RESULTS AND DISCUSSION

Compatibility of PMSEA and PMSMA with PVC

A rough guideline for the compatibility of the shell copolymers, PMSMA and PMSEA, with PVC may be discussed in terms of the solubility parameter[5].

The solubility parameter δ_{sm} of a mixed solvent was calculated by

$$\delta_{\mathrm{sm}} = \phi_1\delta_1 + \phi_2\delta_2 \tag{1}$$

where ϕ_1, ϕ_2 and δ_1, δ_2 are the volume fractions and solubility parameters of solvents 1 and 2, respectively. If the water ($\delta_{\mathrm{s}} = 47.7$), methanol ($\delta_{\mathrm{s}} = 29.6$), cyclohexane ($\delta_{\mathrm{s}} = 16.7$) and hexane ($\delta_{\mathrm{s}} = 14.9$) were used as precipitating agent, the solubility parameter of the copolymer may be calculated by the following equation:

$$\delta_{\mathrm{p}} = \frac{1}{2n}(\delta_{\mathrm{sm}}h_1 + \delta_{\mathrm{sm}}\mathrm{l}_1 + \cdots + \delta_{\mathrm{sm}}h_n + \delta_{\mathrm{sm}}\mathrm{l}_n) \tag{2}$$

where n is the number of precipitating agents, $\delta_{\mathrm{sm}}h$ is the solubility parameter of mixed solvent that was determined by a precipitating agent of high δ, $\delta_{\mathrm{sm}}\mathrm{l}$ was determined by a precipitating agent of low δ. From the experimental turbidity titration, the solubility parameter δ_{p_1} of the PMSEA copolymer was estimated; it is 20.10 ($\mathrm{J}^{\frac{1}{2}}\,\mathrm{cm}^{-3/2}$). The solubility parameter δ_{P} can also be calculated from the molar attraction constant of a constitutive group:

$$\delta_{\mathrm{P}} = \frac{\sqrt{\sum F_{\mathrm{pi}}^2}}{\sum V_{\mathrm{pi}}} \tag{3}$$

where F_{pi} is the molar attraction constant of a molecular constitutive group, V_{pi} is the molar volume of the constitutive group. From equation (3), we obtained δ_{p} as 20.20 ($\mathrm{J}^{\frac{1}{2}}\,\mathrm{cm}^{-3/2}$). These δ_{P} values are nearly equal to the solubility parameter of PVC, 19.2–22 ($\mathrm{J}^{\frac{1}{2}}\,\mathrm{cm}^{-3/2}$), so that PMSEA is expected to be miscible with PVC.

In the same way, we can obtain the solubility parameter δ_{p} of PMSMA: it is 19.61 ($\mathrm{J}^{\frac{1}{2}}\,\mathrm{cm}^{-3/2}$). Therefore, PMSMA is expected to be miscible with PVC. Thus, both shell copolymers are expected to be miscible with PVC.

The morphology of mixtures of these core–shell copolymers with PVC shows that the compatibility is good. Although the particles of dried core–shell copolymers are usually larger than 0.1 mm (diameter), the morphology of the mixtures is uniform. The morphology of PBA/PMSMA with PVC is shown in *Figure 1*. Although the PVC could not be dissolved in acetone, PBA/PMSEA and PBA/PMSMA copolymers could be dissolved by acetone, but the holes did not appear on the surface of the mixture samples after they were placed in

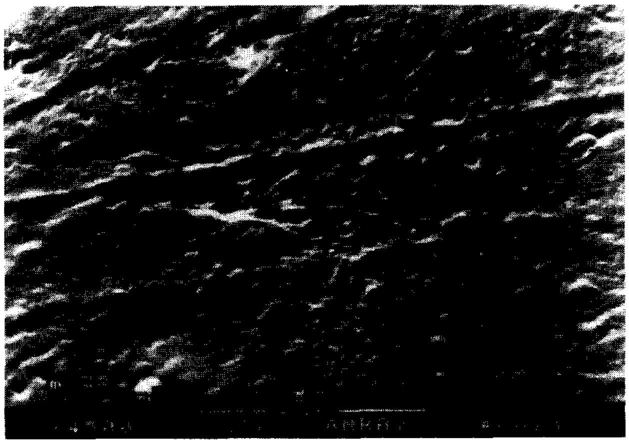

Figure 1 Scanning electron micrographs of a mixture of PBA/PMSMA copolymer with PVC (1/10)

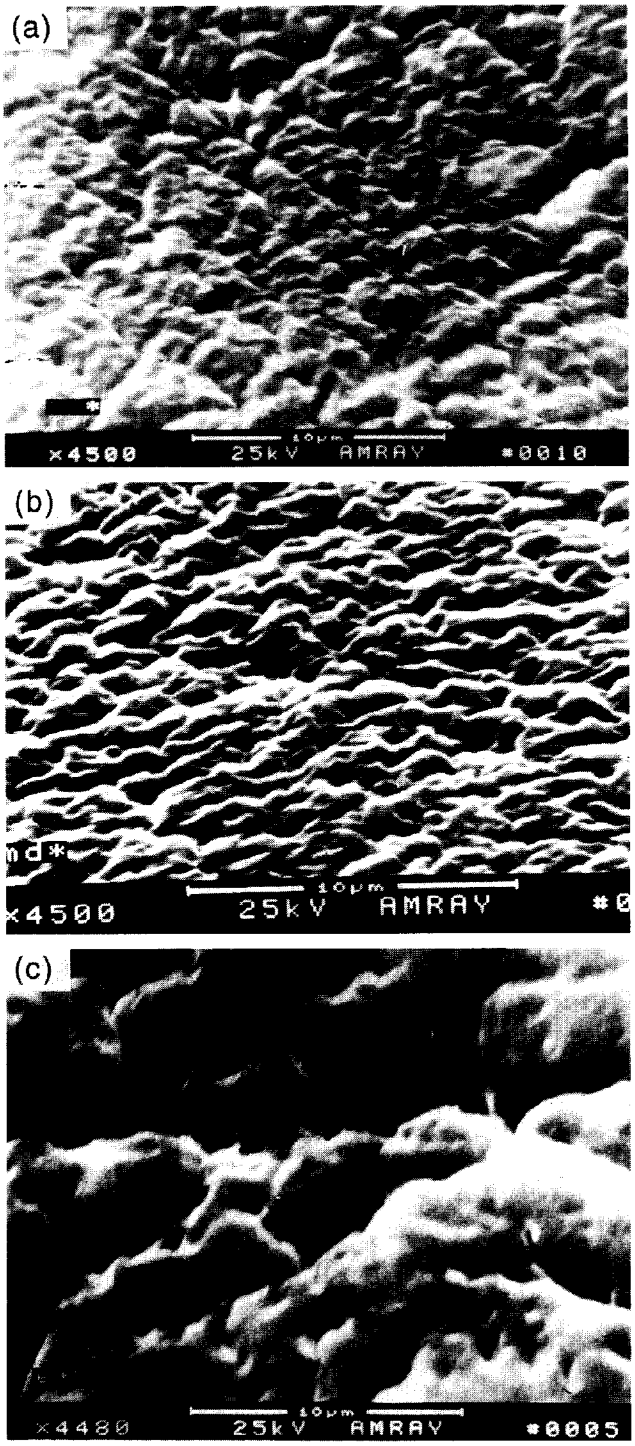

Figure 2 Scanning electron micrographs of mixture samples after placing in acetone for 8 h: (a) PVC; (b) PBA/PMSMA–PVC (1/10); (c) PBA/PMSEA–PVC (1/10)

acetone for 8 h. The samples of blend and PVC were all swollen by acetone, and the original plane shape disappeared (*Figure 2a, b, c*).

Figure 3 is the dynamic mechanical graph of these blends. It is obvious that, in the range of measured concentrations, a satisfactory miscibility is exhibited by systems PVC–PBA/PMSEA and PVC–PBA/PMSMA.

The glass transition temperature (T_g) of PBA, PMSEA, PMSMA and PVC is −56, −8, 9 and 81°C, respectively, but the dynamic modulus G' drops by one step only[2].

Rheological behaviour of blends of PBA/PMSMA and PBA/PMSEA with PVC

The experimental specimens were prepared using the recipes: to five mixtures of PVC (100 parts), TLS (3 parts), DLS (2 parts), wax (0.2 part) and BS (2 parts) was added PBA/PMSMA or PBA/PMSEA in 0, 4, 6, 8 and 10 parts, respectively, and the experiments were numbered as 0, 1, 2, 3 and 4 successively.

The experimental temperature was fixed at 180°C, with experimental loads of 70, 80, 90 and 100 kg, respectively (experimental loads of PVC–PBA/PMSEA blend were 85, 90, 95 and 100 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:

$$\tau_w = \frac{Pr}{2L} \tag{4}$$

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

The efflux rate is given by

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

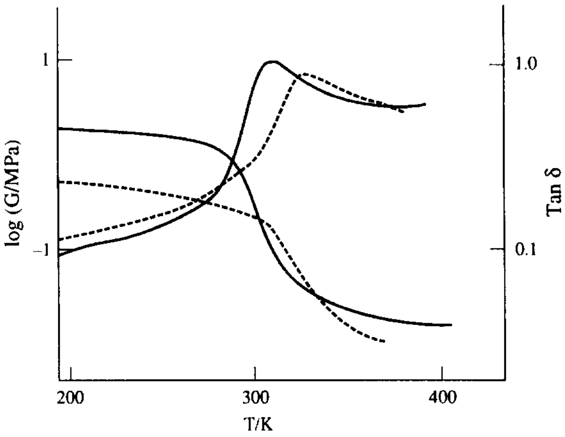

Figure 3 Dynamic mechanical graphs for the mixtures of PBA/PMSMA–PVC and PBA/PMSEA–PVC: (-----) PBA/PMSMA–PVC (1/10); (——) PBA/PMSEA–PVC (1/10)

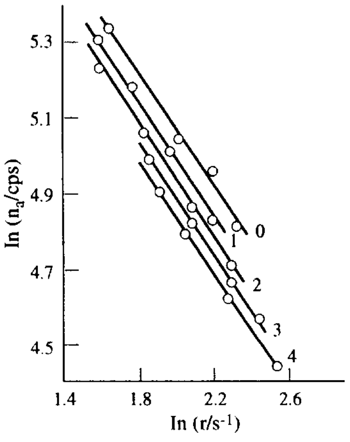

Figure 4 Apparent viscosity η_a of the mixture melt *versus* shear rate $\dot{r}$ for the mixture of PBA/PMSMA with PVC at 180°C (specimens 0, 1, 2, 3 and 4)

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

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

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

The apparent viscosity is given by

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

Plots of $\ln \eta_a$ *versus* $\ln \dot{r}_w$ are given in *Figures 4* and *5*. As is seen from these figures, the apparent viscosity η_a decreases with increasing shear rate. It is shown that the flow behaviour of this mixture in the melt is the behaviour of a pseudoplastic liquid. When the PBA/PMSMA and PBA/PMSEA copolymers were used as a processing aid for PVC, the melt viscosity decreased with increasing amounts of the aid. When 4% PBA/PMSMA or PBA/PMSEA was used as processing aid, the melt viscosity η_a could be lowered by 3×10^4 to 6×10^4 poise, and, therefore, the processing temperature for hard PVC could be lowered. As is seen from *Figure 3*, these blends have a lower T_g than PVC. The T_g of PVC is usually 81°C, but when 8% copolymer was used as processing aid, the T_g of blends of PVC–PBA/PMSMA and PVC–PBA/PMSEA were 52 and 37°C, respectively. When 2% copolymer was used, the T_g of the blends were 75 and 62°C, respectively. However, in practice, when only a small amount (1–2%) of processing aid was added, the T_g, hardness and other mechanical properties incurred only small losses, and the processing operations were significantly facilitated. From these T_g, we know that the blend of PVC–PBA/PMSEA is softer than the blend of PVC–PBA/PMSMA. It is also the reason that the blend of PVC–PBA/PMSEA is swollen to a greater extent by acetone than the blend of PVC–PBA/PMSMA (*Figure 2*).

Mechanical properties and morphology

The notch impact strength of these specimens for mixing different amounts of PBA/PMSMA is shown in *Figure 6*. As is seen from *Figure 6*, the impact strength increases with increasing amounts of PBA/PMSMA used. Therefore, PBA/PMSMA 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, which increases the impact strength of hard PVC, also increases the processing viscosity η_a[6].

The properties of PBA/PMSEA were different from those of PBA/PMSMA. When the added amount of PBA/PMSEA was less than 4%, the impact strength of the blend was higher than that of hard PVC, but when

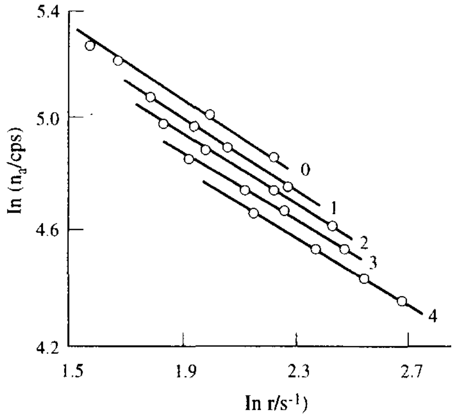

Figure 5 Apparent viscosity η_a of the mixture melt *versus* shear rate $\dot{r}$ for the mixture of PBA/PMSEA with PVC at 180°C (specimens 0–4)

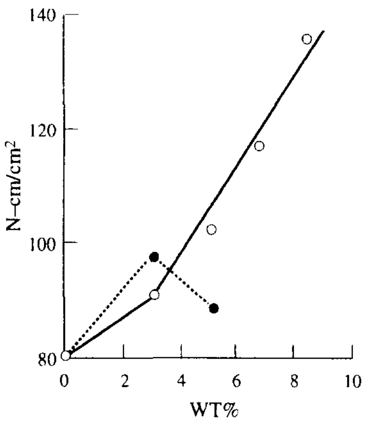

Figure 6 Relationship between impact strength and the ratio of copolymer to PVC: (———) PBA/PMSMA–PVC; (-----) PBA/PMSEA–PVC

Figure 7 Scanning electron micrographs of impact breaking surface for the samples: (a) PBA/PMSMA–PVC; (b) PBA/PMSEA–PVC

Table 1 Tensile strength and hardness of improved PVC

Specimen		0	1	2	3	4
Tensile strength	I	3410	4268	4034	3912	2668
($N\,cm^{-2}$)	II		3700	3690	3542	3357
Hardness	I	25.5	24.8	23.7	23.2	22.2
($kg\,mm^{-2}$)	II		24.0	23.4	22.9	22.1

Note: I is the blend sample of PBA/PMSMA with PVC, and II is the blend sample of PBA/PMSEA with PVC

the added amount of PBA/PMSEA was over 5%, the impact strength was lessened.

Figures 7a and *b* are the SEM graphs of impact breaking surface for samples of PVC–PBA/PMSMA and PVC–PBA/PMSEA systems. As is seen from *Figure 7a*, the breaking surface is not so clear cut; there are so many fine holes on the impact breaking surface. The PBA/PMSMA copolymer is a pliable component in this blend; it has good compatibility with PVC. When this material was subjected to impact, the copolymer particles became centres of stress, absorbed significant amounts of energy in this region and prevented break of the materials[8,9].

As opposed to blend (a) (*Figure 7*), relatively large holes appear on the impact breaking surface of blend (b). It has the character of a soft material. This was also explained by dynamic mechanical analysis. When a relatively large amount of PBA/PMSEA copolymer was added to PVC, the blend had a lower T_g and became a soft material. Therefore, a small amount of PBA/PMSEA can only be added for use as a processing aid.

The tensile strength and hardness for improved PVC by PBA/PMSMA and PBA/PMSEA are shown in *Table 1*. As is seen from *Table 1*, the tensile strength and hardness decrease with increasing the amount of PBA/PMSMA and PBA/PMSEA. These results are similar to those for a general commercial processing aid and resistant impact aid[2,6].

CONCLUSIONS

1. The copolymers of PBA/PMSEA and PBA/PMSMA have good compatibility with PVC; their solubility parameters are close to the solubility parameter of PVC.
2. The PBA/PMSMA and PBA/PMSMA can be used as processing aids for hard PVC, which can decrease the processing temperature and melt flow viscosity of hard PVC, but also can increase its impact strength.
3. When these copolymers were mixed with PVC, the tensile strength and hardness decreased. The added amount of PBA/PMSEA and PBA/PMSMA are 2–4% and 3–8%, respectively.

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 Plast.* 1992, **1**, 26
5 The Group for Polymer Chemistry, Department of Chemistry, Beijing University, 'Physical Experiments in Polymer Science', Beijing University Publishing Co., 1983, p. 196
6 Lu, M. J. and Wu, S. H. *Plastic Technol.* 1989, **1**, 7
7 Arai, T. 'A Guide to the Testing of Pheological Properties with Koka Flow Tester', Maruzen Co., Tokyo, 1958, p. 16
8 Elias, H. G. 'Macromolecules, 1', Plenum, New York, 1977, pp. 452–456
9 Clas, S. D. and Elsenbekg, A. *J. Polym. Sci.* 1984, **22**, 1529