Polymer Journal, Vol. 34, No. 3, pp 132—137 (2002)

A Study on Preparation of Functionalized Ultra-Fine Polypropylene Powder through a Mechanochemical Method

Yuan LIU and Qi WANG†

The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

(Received September 12, 2001; Accepted January 31, 2002)

ABSTRACT: In this paper, a mechanochemical method was established to prepare functionalized ultra-fine polypropylene powder. Through pan-milling by a self-designed pan-type mechanochemical reactor, polypropylene (PP) was finely pulverized, during the process, Inorganic peroxide solution was sprayed onto the PP powder surface to realize its rapid functionalization taking advantages of the mechanochemical effects caused by milling. Analysis results of electron spectroscopic chemical analysis (ESCA) show the PP ultra-fine powder prepared by this method can obtain over 0.1 oxygen content (O/C). Some factors influencing functionalization degree, including concentration, spraying amount of Inorganic peroxide solution and milling temperature, were discussed. Besides, the degradation of PP during this process was investigated.

KEY WORDS Ultra-Fine Powder / Functionalization / Polypropylene / Mechanochemistry / Pulverization /

With the development of polymer science, polymer ultra-fine powder techniques have attracted much attention because of its wide application in many fields, such as antiblocking, matting agent, ink additive, cosmetics, ultra-fine filler, powder coating and so on.[1,2] Polymer ultra-fine powder can be prepared by chemical methods[3–6] including emulsion polymerization and dispersion polymerization, and physical ones including solution-crystallization-precipitation process[7,8] and mechanical pulverization. Among the methods, mechanical pulverization has obvious advantages such as a simple process, big capacity, relatively low cost and friendly to environment. However, for polymer materials, due to special heat sensitivity and viscoelasticity, during pulverizing, a considerable part of exterior energy can be consumed through variation of conformation and movement of their molecular chains. Accordingly they cannot be pulverized as easily as most inorganic materials. By this, it is not difficult to understand why general pulverization equipment, such as ball mill, roller mill, etc., show inefficiency in pulverizing polymers at an ambient temperature. In order to realize ultra-fine pulverization of polymers, deep cryogenic through liquid nitrogen is usually adopted during pulverizing, which can obtain polymer powders with an average particle diameter of 100 μm below, however, high expenditure in such a process restricts its application. Therefore, developing a ultra-fine pulverizing technique at an ambient temperature, whether in theories or in practice, is valuable.

Polyolefin, is important commodity plastics of the highest output worldwide among all polymer products. Because without polar functional groups in the molecular chains, they show a chemical inertia, which makes their ultra-fine powder can be applied to some special fields. An typical example is anticorrosion powder coating widely used on plastics coating steel sheet and tube, if the particle diameter reaches 15–40 μm, it can realize the thin-film coating on matrix surface, which will save not only much energy, but also a lot of materials. However, the chemical inertia of the polyolefin ultra-fine powder also make it difficult to obtain a strong adhesion between the coating film and steel matrix and the coating film easily falls out to cause the protective coating layer out of service. So, for polyolefin ultra-fine powder, except the requirement of particle diameter, the functionalization is also in need, namely, enhancing the polarity of polyolefin through inducing some polar functional groups onto macromolecular. Although a lot of research work[9–13] on functionalization of polyolefin were done in the past, the functionalization research specially aiming at ultra-fine polyolefin powder, particularly those simultaneously realizing the functionalization in the pulverizing process was seldom reported.

Polymer solid-phase mechanochemistry is a frontier science based on solid-phase mechanics and polymer chemistry. Solid-phase mechanochemical effect, as a combination of mechanical effect and chemical effect, is a nonequilibrim physics-chemistry phenomenon, induced by stress in solid-phase of polymers, such as stress activation, stress degradation, and stress synthesis.[14] Because of above properties, polymer solid-phase mechanochemistry actually offers a new route

†To whom correspondence should be addressed.

for the preparation and modification of polymer materials. In our previous articles,[15,16] a self-designed pan-type equipment was used to conduct solid-phase mechanochemical reaction between polyolefin and polar monomer such as maleic anhydride (MAH) and *N*-(Hydroxymethyl)acrylamide (HMA), a relatively high grafting ratio was obtained. The pan-type was also applied to prepare ultra-fine composite powder, say, polyamined(PA6)/polypropylene(PP) and PP/iron system, it was found a sub-micrometer phase domain in above composite system could be obtained through the pan pulverizing and blending in solid state. These studies indicate the pan-type milling equipment can be applied to not only mechanochemical reaction of polymers, but also their ultra-fine pulverization and high degree mixing. In this paper, the comprehensive effects were made full use of to establish a new method to prepare ultra-fine functionalized polyolefin powder, namely, the ultra-fine pulverization and functionalization are simultaneously conducted through inorganic peroxide solution spraying during milling, by this, the process and modification is integrated.

EXPERIMENTAL

Materials

PP, F401, with an average pellet diameter of 2–4 mm, was supplied by QiLu Petrochemical Co. of China. Potassium peroxydisulfate ($K_2S_2O_4$), AR, was obtained from Shanghai AiJian Reagent Co. of China.

Equipment

A hand sprayer. It was obtained from XiFei sprayer Co. of China.

A horizontal-axis pan-mill mechanochemical reactor.[17,18] The self-designed pan-type equipment can realize pulverizing, mixing and stress reaction of solid mass. Its key part is constituted by a pair of inlaid pans, which are made of wear-resistant metal and specially treated on the surface. Figure 1 shows its detailed interior structure. A chain transmission system and a screw pressure system is set to regulate the rotation speed of moving pan and imposed load respectively, which can strictly control two major dynamic parameters, velocity and force during milling. Cooling water flows through the hollow interior of the pan to take away the heat generated during milling, by controlling the flow, milling temperature is adjustable. Milling process of solid mass in the equipment can be described as follows, the materials are fed to the center of the pan from the inlet, driven by shear force, move along a spiral route toward edge of the pan till come out from the outlet, thus one cycle of milling is finished.

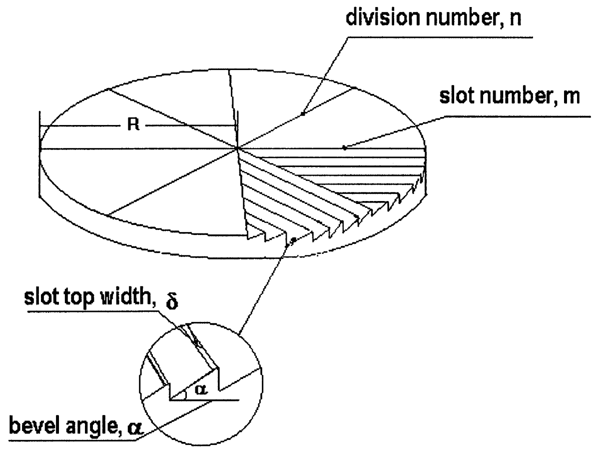

Figure 1. Schematic diagram of milling-pan.

Preparation of Functionalized Ultra-Fine PP Powder

Original PP particles were pulverized to fine powder in the pan-type mechanochemical reactor for 10 cycles with a rotation speed of 30 cycles min^{-1}, then a certain concentration and amount of $K_2S_2O_4$ solution was sprayed onto the powder surface, further pulverizing to prepare functionalized ultra-fine PP powders. During the process, the milling temperature was controlled by adjusting cooling water flow. Above powders were washed by water to remove the residual peroxide and a certain amount of antioxidant was added. Then the final product was obtained.

Characterization

Grainsize Analysis. The particle size and distribution of the PP powder was measured by a laser light scattering granulometer (Shimadz 2001, Japan).

Electron Spectroscopic Chemical Analysis (ESCA). The binding forms of oxygen and its content (O/C ratio) of powder sample was determined by ESCA energy spectrometer (XSAM 800, U. K.). The analysis chamber was kept at constant vacuum (10^{-9} torr) and pass energies of the electron analyzer were set at 25 eV during the experiment.

Contact Angle Measurements. Contact angle measurements were made with a Contact Angle-Meter (Erma G-1, Japan). The original PP, alone milled PP powder and functionalized PP powder were compression-molded to films and pure water was used as testing liquid.

Molecular Weight Measurement. The viscosity-average molecular weight of PP powder was tested by viscometry according to the following equation:[19]

$[\eta] = 9.6 \times 10^{-2} \overline{M}_\eta^{0.63}$ (dimethyl benzene, 110°C)

Table I. ESCA analysis of C_{1S} of alone milled PP and functionalized ultra-fine PP powder

	Peak position C_{1S}	Peak area (cps∗eV)	The forms of binding oxygen	Oxygen content (O/C)
	285.1	9533.8	C–C	
PP milled alone	287.9	207.9	C=O	0.034
	289.8	142.7	O–C=O	
	285.1	9798.3	C–C	
Functionalized ultra-	288.1	807.1	C=O	0.119
fine PP powder	289.7	359.8	O–C=O	

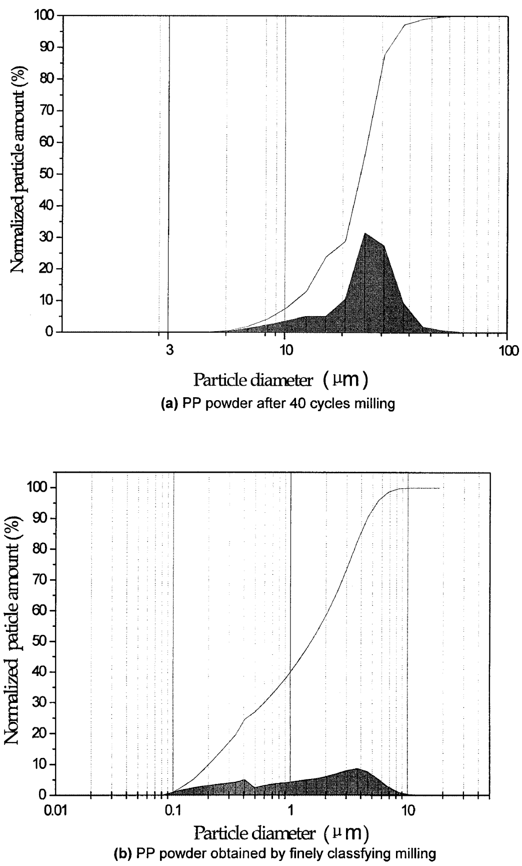

Figure 2. Particle size distribution of ultra-fine PP powder.

RESULTS AND DISCUSSION

Ultra-Fine Pulverization of PP During Pan-Milling

Figure 2 shows the particle size distribution of functionalized ultra-fine PP powder. The original particle size of PP was about 2–4 mm, after 40 cycles pan-milling at an ambient temperature (30°–40°C), its average particle diameter reduced to 28 μm, and the particle diameter distribution mainly ranged from 10 μm to 40 μm. Through a fine classification, ultra-fine powder was obtained. Figure 2 shows the particle size distribution of the finest powder product obtained by this method. It can be seen about 40% PP powder reach submicrometer dimension. Pan-type mechanochemical reactor could pulverize PP effectively, which is attribute to its unique mechanical structure generating an integral and lasting mechanical effect during milling, as can be explained from two sides as follows. Firstly, between two pans, all materials are under a strong shear force, pressure and hoop stress applied by the pans, just like being sheared by a three-dimensional scissors, which makes solid mass easier be broken down and split. Secondly, although the diameter of the pan (40 cm) is relatively short, because moving route of materials is a spiral trajectory,[18] the actual moving distance is very long, which is equal to prolonging the residence time of mass in the stress field, therefore, favoring pulverization of polymer materials.

Table II. Contact angle analysis of PP samples

	Film made from original PP	Film made from alone milled PP powder	Film made by functionalized PP powder
Contact angle	87°	81°	57°

Functionalization of PP Powder during Milling through $K_2S_2O_4$ Solution Spraying

Figure 3 is the ESCA analysis results. From it, it can be seen that the C_{1S} binding energy of carbon–carbon bond of PP molecular chain is 285.1 ev. For functionalized PP powder, because of the introduction of a great number of oxygen–containing functional groups, its C_{1S} spectrum appeared a big tailed peak on the side of higher binding energy. This accorded with that the O_{1S} spectrum of functionalized PP powder had a much bigger peak area than that of original PP. The peak fitting analysis of C_{1S} binding energy spectrum (Table I) shows the O/C of functionalized PP powder system reached 0.119, much higher than that of PP milled alone, and the binding forms of oxygen mainly were C=O at 288.1 ev and O–C=O at 289.7 ev.[20]

Table II shows the contact angle of the compression-molded film from original PP, alone milled PP and functionalized ultra-fine PP powder respectively. Compared with that of the original PP, The contact angle of the alone milled PP basically kept unchanged. However for functionalized ultra-fine PP, the contact angle decreased to 57°, which shows a remarked increase of polarity.

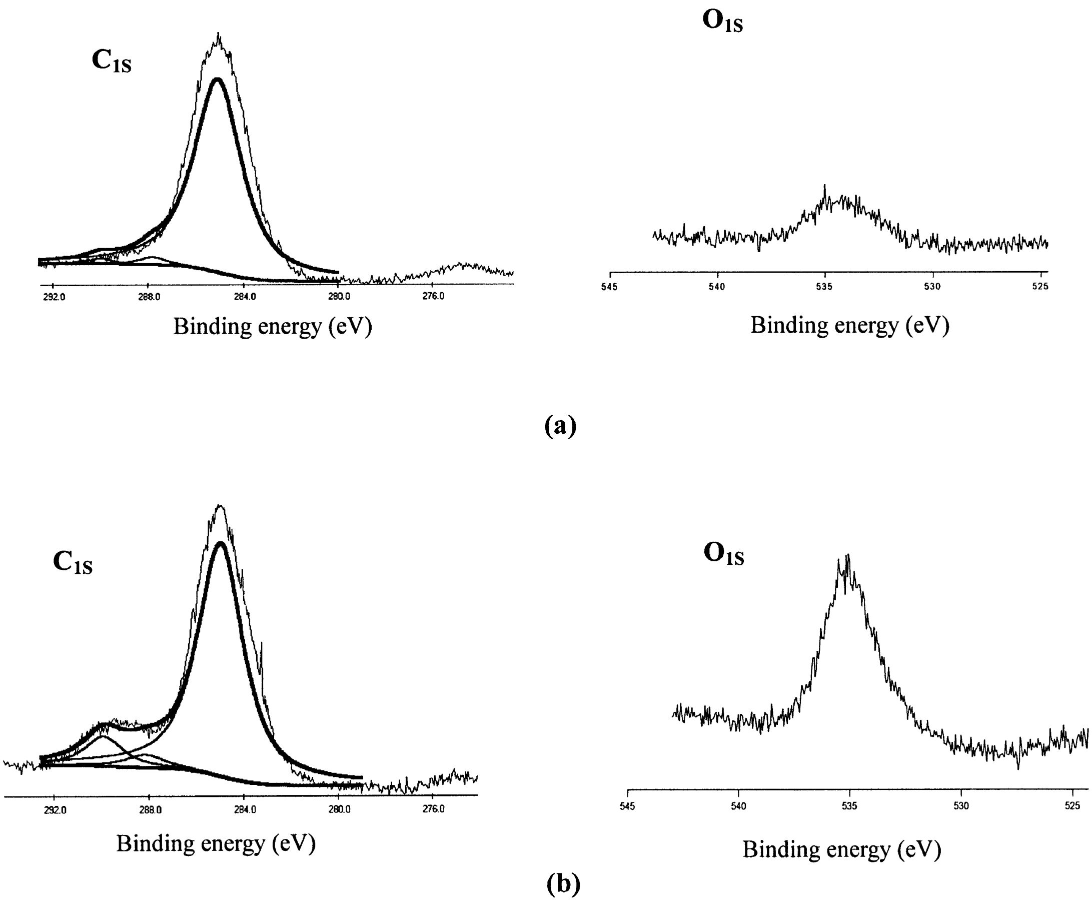

Figure 3. C_{1S} and O_{1S} binding energy spectra of PP powder after 40 cycles milling (a: alone milled PP powder, b: functionalized PP powder).

Usually, it is deemed that the oxidation on polyolefin in existence of inorganic peroxide is a slow and complicated process, which is difficult to be controlled. In addition, inorganic peroxide solution is a aqueous system, poor wetting with the polyolefin. From the viewpoint of thermodynamics, there is no compatibility between them. C. E. M. Morris[21] ever tried to treat polyolefin surface with inorganic peroxide to improve the adhesion between the material and other matrix, however, a obvious increase of polar functional groups was not found, which illuminated that interaction between polyolefin and inorganic peroxide solution was very weak in a simple commix. By the technique of inorganic peroxide solution spraying during milling, a strong interaction between them was proved to take place according to above ESCA and contact angle analysis. This may be explained as follows. Firstly, spraying favors an even dispersion of inorganic peroxide solution in the PP powder system. Secondly, pan-milling is a dynamical controlling process, which urges compelling compatibilization of the two constituent through a intensive solid-phase blending. Thirdly, pan-milling is not only a simple pulverizing process, but also a typical mechchanochemical process. On one hand, with the breaking of PP particle, its surface area and energy increase rapidly, which favors peroxide solution absorbing on PP powder surface, on the other hand, the strong shear force induce the changes of polymer supermolecular structure, orientation of macromolecular chains and distortion or deformation of chemical bonds to cause macromolecular stress activation.[14] In the state, macromolecular chains obtain much higher reactant activity than in usual state, so more easily interact with peroxide to induce oxygen-containing functional groups.

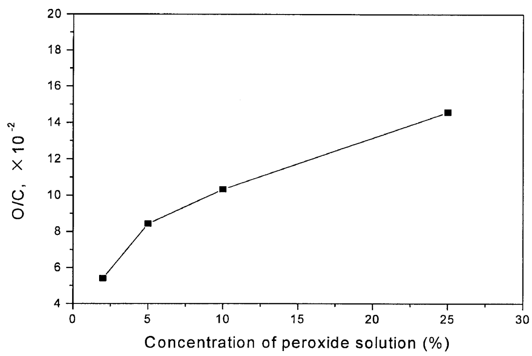

Figure 4. Influence of concentration of peroxide solution on O/C ratio of PP ultra-fine powder (spray amount: 30 mL/100 g, milling temperature: 40–45°C).

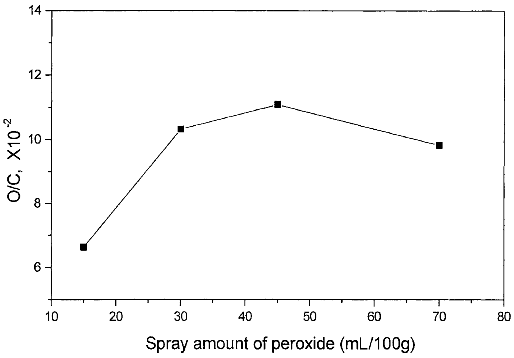

Figure 5. Influence of spray amount of peroxide solution on O/C ratio of PP ultra-fine powder (peroxide concentration: 10%, temperature: 40–45°C).

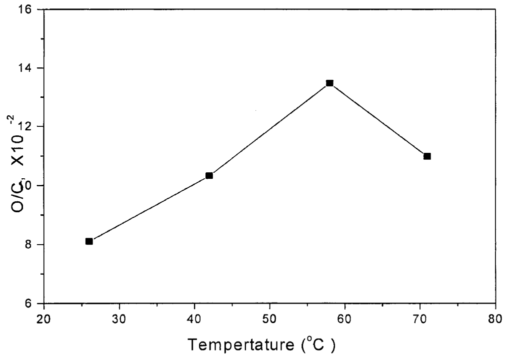

Figure 6. Influence of milling temperature on O/C ratio of PP ultra-fine powder (peroxide concentration:10%, spray amount: 30 mL/100 g).

The Influence of $K_2S_2O_4$ Solution Concentration and Spraying Amount on Oxygen Content of the Ultra-Fine Powder

From Figure 4, it can be seen that the oxygen content of the ultra-fine powder enhanced with the increase of $K_2S_2O_4$ solution concentration when spraying amount is set and the milling temperature ranges from 40–45°C. When a concentration of 25% was adopted, the oxygen content could reach 0.14. However, too high concentration may cause excessive oxidation of PP and deteriorate its properties. For example, when the oxygen content reaches 0.14, the color of PP ultra-fine powder changes from white to yellow, which will decrease the commercial value of the product. So it is reasonable to adopt a suitable concentration of peroxide solution. When the milling temperature region is the same but the concentration is fixed as 10%, the spraying amount shows a complicated influence on the oxygen content of PP powder (Figure 5), which presents an increasing tendency when spraying amount is below 45 g/100 mL, but a deceasing tendency when the spraying amount is beyond this. The reason may be that a big spraying amount makes the powder system contain a great deal of interstitial water. The water may form water film easily transferring on the surface of PP powder and generated lubricating effect, released the shear force exerted on the mass during milling. The effects directly cause the weakening of mechanochemical effects and the decrease of macromolecular chains activated by stress, and finally lead to the decrease of functionalization degree of PP powder system.

The Influence of Milling Temperature on Oxygen Content of the Ultra-Fine Powder

Figure 6 shows the effect of milling temperature on oxygen content, below 60°C, O/C ratio increases with increase of temperature. However, the ratio declines when temperature beyond 60°C. On one hand, at a higher temperature, the peroxide bears higher activity, interacts with the PP molecular more easily. On the other hand, generally, temperature has negative effect on mechanochemical reaction, because higher temperature will increase the flexibility of macromolecular chain, unfavorable to its stress activation. For example, for the solid-phase mechanochemical grafting of MAH onto polypropylene by the equipment,[13] the grafting ratio decreases with the increase of milling temperature, which shows the number of macromolecular radical induced by stress declines at higher temperature. The above comprehensive effects of milling temperature lead to the oxygen content reaches the maxim value at a moderate temperature (about 60°C). Beside, a high temperature will cause the powder surface softening and viscous. In such case, it is more difficult to realize the ultra-fine pulverization of polymer due to adhesion and agglomeration of polymer powders. Accordingly, a relatively lower milling temperature should be adopted on the premise of obtaining expected oxygen content.

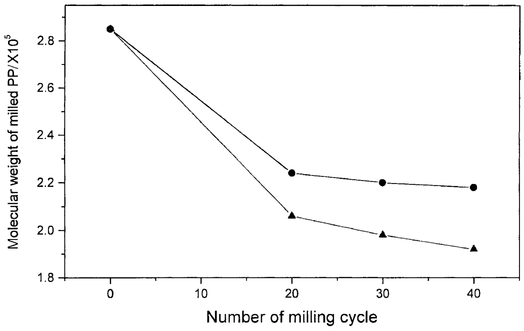

Figure 7. Degradation of PP in the milling process (● without spraying peroxide solution, ▲ spraying peroxide solution).

Degradation of PP

Figure 7 shows the variation of viscosity-average molecular weight of PP powder with the increase of milling cycles. It can be seen, for both the alone milled PP powder and functionalized PP powder, their molecular weight decreased to a certain degree during milling. Compared with the former, the molecular weight of functionalized PP powder is lower on the same milling cycles. This shows that peroxide accelerates the degradation of PP. Despite different degradation degree for the two powder systems, however, from Figure 7. It is clear that the decreasing tendency of their molecular weight is similar, namely, molecular weight decreased rapidly in initial milling stage, with the milling degree increase, the decreasing tendency let down, and gradually come certain value, demonstrating that the mechanochemical degradation exist a limit during milling.

CONCLUSION

The self-made pan-type mechanochemical reactor can effectively pulverize the polymer materials. Through milling, the PP powder with a average particle size of 28 μm was prepared. After fine classification, the ultra-fine powder of a average particle diameter 1.4 μm was obtained.

Taking advantages of the mechanochemical effects, spraying inorganic peroxide solution during milling can rapidly interact with PP chains activated by stress and form oxygen-containing functional groups, mainly O–C=O and C=O.

The oxygen content of functionalized ultra-fine powder increase with the increase of peroxide solution concentration. The spray amount and milling temperature has complicated influence on oxygen content, and their moderate values favor enhancing the oxygen content.

As a mechanochemical method to prepare functionalized ultra-fine PP powder reported in this paper, this co-milled ultra-fine pulverizing and functionalizing process, has the advantages such as a simple, high efficiency and easy to be commercialized.

Acknowledgment. The research is subsidized by the Special Funds for Major State Research Projects of China (G1999064809).

REFERENCES

1. I. Yoshasu, T. Masuyuki, K. Teruo, and K. Yukio, Japanese Patent S63-311264 (Jun. 12, 1987).
2. N. Shoichi, H. Saburro, and H. Shinji, Japanese Patent S63-10671 (Jun. 30, 1986).
3. J. Ugelstad, P. C. Mork, and K. H. Kaggerud, *Adv. Colloid Interface Sci.*, **13**, 101 (1980).
4. A. J. Paine, W. Luymes, and Mcnulty, *Macromolecules*, **23**, 3104 (1990).
5. M. A. Winnik, *J. Polym. Sci., Polym. Lett.,* **23**, 103 (1983).
6. A. Guyot, in "Comprehensive Polymer Sciensle", Pregamon Press, Oxford, 1989, vol. 4, p 16.
7. Y. Takashi, Japanese Patent, S62-101628 (Oct. 29, 1985).
8. J. Smith., *Drug Cosmet. lnd.*, **139(2)**, 79 (1986).
9. P. Ghosh and A. K. Chattopadhyay, *Polymer*, **39**, 193 (1998).
10. J. X. Thomas and A. W. Charles, *Polym. Prepr.*, (*Am. Chem. Soc., Div. Polym. Chem.)*, **36(2)**, 251 (1995).
11. V. Khunova and Z. Zamorssky, *Polym.-Plast. Technol. Eng.*, **23**, 289 (1993).
12. I. Barnikol and W. K. R. Barnikol, *Makromol. Chem.*, **137**, 111 (1970).
13. Q. Wang and C. L. Liu, at 14th Meeting of Polymer Processing Socitey, Yokohama, Japan, June 8–12, 1998, p 633.
14. R. S. Porter and A. Casele, *Polym. Eng. Sci.,* **9**, 467 (1987).
15. C. S. Liu and Q. Wang, *J. Appl. Polym. Sci.*, **78**, 2191 (2000).
16. Z. Chen, C. S. Liu, and Q. Wang, *Polym. Eng. Sci.*, **47**, 1187 (2001).
17. X. Xu, Q. Wang, X. A. Kong, and J. G. Huang, *Plast. Rubb. Compos. Proc. Appl.,* **25**, 152 (1996).
18. Q. Wang, J. Z. Cao, G. J. Li, and X. Xu, *Polym. Int.*, **41**, 245 (1996).
19. J. Brandrup and E. H. Immergut, "Polymer Handbook", 2nd ed, John Wiley & Sons, Inc., New York, N.Y., 1975, chapt. 1V-1-1V-32.
20. D. M. Brewis and D. Briggs, *Polymer*, **22**, 7 (1981).
21. C. E. M. Morris, *J. Appl. Polym. Sci.*, **14**, 217 (1970).