

Micron-Sized Polymeric Microsphere by Suspension Polymerization

MASAFUMI KAMIYAMA,^{1,*} KIKUHIKO KOYAMA,² HIDEOMI MATSUDA,³ and YOSHIKI SANO³

¹Technical Research Laboratory, Tomoegawa Paper Co. Ltd., 3-1 Mochimune Tomoemachi, Shizuoka, 421-01 Japan;

²Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Nagano, Japan;

³Department of Fine Materials Engineering, Faculty of Textile Science, Shinshu University, Nagano, Japan

SYNOPSIS

A new suspension polymerization process that generates narrow-size distribution and spherical particles in the range of 3–10 microns is described. In the new process, the monomer and water phases are held in separate vessels and fed at an accurate rate to a mechanical disperser, where small, uniform droplets of monomer are formed. The monomer droplets are then fed to a reaction vessel where the monomer is polymerized. The size of the polymerized particles can be effectively controlled by adjusting the disperser speed. A scanning electron microscope was employed to show the spherical nature of the particles. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Micron-sized particles in the range of 1–10 microns have attracted considerable attention as microsphere functional polymers by biomedical, microelectronics, and informational industries. Currently, industrial technology to produce particles in this size range has not been established. However, manufacturing technology of polymeric microspheres, such as emulsion and latex or polymer beads, have been utilized on an industrial scale for many years. These processes render polymer particles for emulsion and suspension polymerization between ca. 0.1 and 1.0 microns and ca. 100 and 1000 microns, respectively.

Several process methods for micron-sized polymer particles, such as seed polymerization,¹ soap-free polymerization,² and dispersion polymerization,³ have been reported. However, these polymerization methods are rather complicated and require numerous time-consuming reaction steps and procedures. Also, the introduction of functional groups, or the control of molecular weight distribution, is extremely difficult with these methods. On the other hand, suspension polymerization has been widely

utilized for industrial production of resins and plastics due to the simplicity of the reaction process and equipment. Suspension polymerization has many advantages, including that (1) a variety of vinyl monomers can be utilized, (2) the polymer particles can be modified by functional groups, and (3) the polymer particles can be generated with various rheological properties. Another advantage is the low contamination of the particle surface with surfactants. The contamination of the particle surface may become a serious design problem for the performance characteristics of the particles. Therefore, a suspension polymerization process could provide a new technology in the polymer industry, if it could be adapted to the production of micron-sized polymer particles.

The suspension polymerization process involves suspending monomers in an aqueous phase to create monomer droplets. The droplets are formed by agitating both the aqueous and monomer phases in a single vessel. Control of the particle size and distribution are necessary for obtaining good polymer microspheres. Vanzo⁴ reported the production of small particles of less than 10 microns, which required the use of relatively high concentrations of dispersant and high agitation rates. A major drawback to this method is the lack of control over particle-size distribution. Almog and Levy⁵ reported the use of both

* To whom correspondence should be addressed.

suspending agents and surfactants in producing small particles. In this case, both emulsion and suspension polymerization proceed simultaneously, which complicates the mechanism and causes a wide particle-size distribution. A typical mechanical agitator for suspension polymerization was felt to be inefficient at generating small, uniform, and well-controlled droplets of less than 10 microns. The size control of such droplets is extremely difficult.⁶ A new system that utilizes suspension polymerization for yielding small, uniform particles of less than 10 microns is described.

PROCESS DESCRIPTION

The new suspension polymerization system that is shown in a schematic view (Fig. 1) was specifically developed for accurately controlled production of small particles. The polymerization system is made up of four parts: (1) a container vessel for an aqueous phase [shown as (A) in Fig. 1]; (2) a container/reactor vessel for the monomer phase (B); (3) a high-speed mill (HSM) or disperser unit (C); and (4) a suspension reaction vessel (D). Suspension agents are premixed with water inside the aqueous vessel A. The monomers and initiators are charged to the monomer vessel B. Both phases are accurately fed to the disperser C by precision gear pumps. The solutions are fed to the disperser with a smooth pulseless flow through a $\frac{1}{2}$ in. id. Teflon pipe. The disperser unit was specifically designed⁷ to disperse the monomer into the aqueous phase, resulting in small uniform droplets. The monomer droplets are stabilized by the suspension agent found in the aqueous phase. The droplets are then fed to the reaction vessel D where the monomer undergoes polymerization. Slow agitation is utilized in the reaction vessel to avoid collapse of the droplets.

The dispersion of the monomer into the aqueous phase is the key step in this process. Dispersion occurs instantly in the restricted area inside the HSM. The HSM was designed to give concentrated and uniform shearing force to both liquid phases.

All experiments were run with the equipment shown in Figure 1. Vessel A is a thermally jacketed 100 L tank with a four-blade paddle agitator. Good agitation was required to ensure complete mixing of the suspension reagents and to prevent their precipitation. Vessels B and D have the same specifications as those of vessel A; however, additional baffles and a condenser were necessary for each. The precision gear pumps were obtained from Kawasaki Heavy Industry Ltd, type BAS10-56.

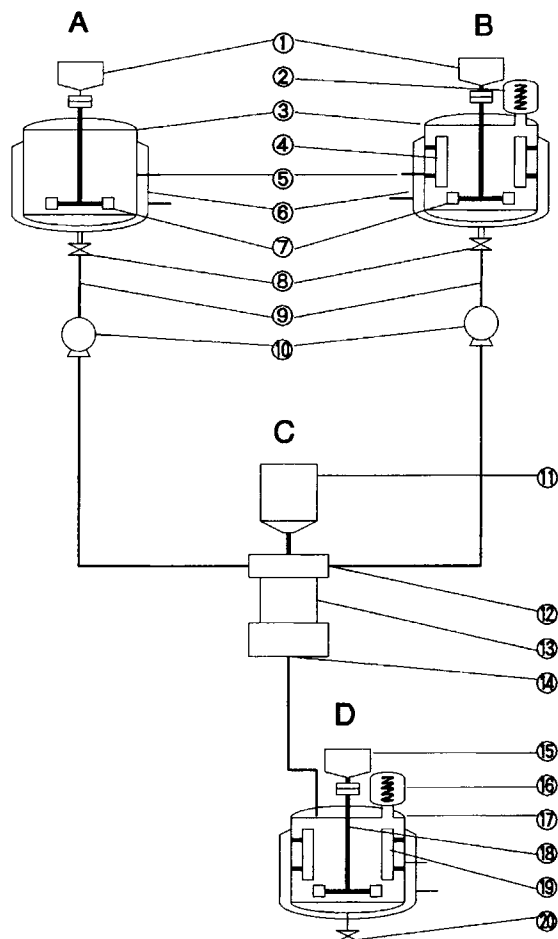


Figure 1 Reactor schematic: (A) continuous-phase vessel; (B) dispersed-phase vessel; (C) disperser (HSM); (D) reaction vessel; (1) motor; (2) condenser; (3) vessel; (4) baffles; (5) thermocouple well; (6) heating jacket; (7) stirrer; (8) valve; (9) $\frac{1}{2}$ in. Teflon tubing; (10) gear pump; (11) motor; (12) liquid inlet; (13) disperser; (14) liquid outlet; (15) motor; (16) condenser; (17) reactor vessel; (18) stirrer; (19) baffles; (20) outlet valve.

EXPERIMENTAL

Reaction Conditions

Reaction conditions were as follows:

Load temperature	25°C.
Agitation speed:	
In disperser	18–41.1 m/s corresponding to a tip speed
In vessel (D)	240 rpm
Initiator	2,2'-Azobis (2,4-dimethylvaleronitrile) (ADVN) 3.8% based on monomer weight

Monomer system	Styrene and <i>n</i> -butylacrylate 4 : 1 based on weight
Dispersants	Calcium phosphate 5% and sodium dodecylsulfate 0.004% both based on water weight
Reaction temperature and time	60°C for 4 h, followed 80°C 3 h
Final conversion	95%

The range of tip speeds investigated for the disperser were within the mechanical limitations of the unit. The initiator, ADVN, was primarily used. Changing the initiator to *N,N'*-azobisisobutyronitrile was investigated, but no effects from this change were observed.

The preferred monomer ratio of styrene to *n*-butylacrylate was 4 : 1. The monomer ratio did not affect the particle size. The monomer ratio and initiator concentration were selected to obtain thermoplastic polymer particles. The particle size did not change when only styrene was used as the monomer. A stepwise increase in the reaction temperature was employed for high conversion.

Reagents

Styrene and *n*-butylacrylate were reagent grade and were treated with 0.1% aqueous sodium hydroxide to remove the inhibitor. The initiators were reagent grade and used without further purification. The dispersant used was commercial-grade calcium phosphate, which is available as a 10% slurry by weight in water. The sodium dodecylsulfate used was

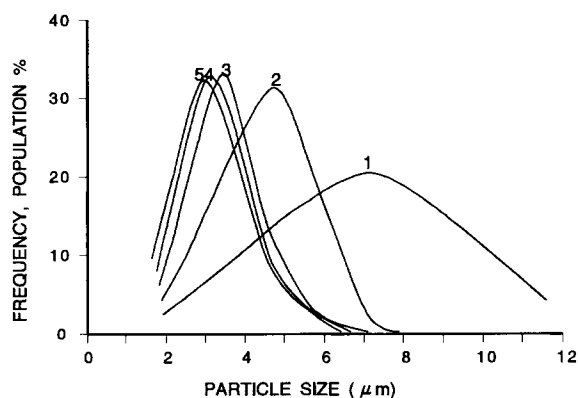


Figure 2 Particle-size distribution. Effect of tip speed. Monomer ratio = 0.25. Tip speed (m/s): (1) 18.0; (2) 23.1; (3) 30.8; (4) 35.9; (5) 41.1.

reagent grade. All experiments run used deionized water.

Molecular Properties of Polymer Particles

Molecular weights were determined by a Waters M600 chromatograph with a UV detector and a System Instrument Co. data processor. The detection wavelength was 268 nm, which corresponds to the adsorption maximum of polystyrene. The column used was Shodex GPC KF-80M packed with polystyrene gel. The separation range of the column is 4×10^7 (molecular weight of polystyrene) at 25°C. Calibration of the column was performed using standardized polystyrenes supplied by Showa Denko KK. The solvent used for elution was THF with a flow rate of 1 mL/min.

Particle Size

Particle size and distribution were determined with a TAI Coulter device by Coulter Electronics. The aperture size on the tube for the Coulter analysis was 75 microns in diameter.

Electron Microscopy

Analysis was performed using a JEOL JSM-T22A scanning electron microscope.

RESULTS AND DISCUSSION

Particle Formation and Stabilization

The process of monomer droplet formation for suspension polymerization has been suggested previously.⁸ In a mutually insoluble monomer and medium system, the monomer will form spherical droplets in the medium. These droplets are generated with the aid of mechanical force and interfacial tension. In these suspended systems, coalescence and break up of the droplets arises simultaneously throughout the agitated medium. It is noted that the process of coalescence was negligible in our system, due to the lack of agitation, once the droplets have been formed and effectively stabilized. The mechanical force that is introduced by the HSM is the dominant factor in deciding the droplet size.

Our findings show that the monomer droplets coalesce negligibly when they are small (< 10 microns) and have uniform-size distribution. One possible explanation is that the uniformity of the droplet size interferes with coalescence. Coalescence tends to

occur in places where there is a pair of large and small droplets. Another reasonable explanation is that the suspension agent acts like a spacer between droplets that inhibits coalescence. The small water-insoluble particles would exist on the surface of the droplets, preventing droplet contact. This spacer mechanism works effectively for considerably smaller droplets because the ratio of surface area/mass is large. The particle size of such a dispersion agent is approximately one-twentieth of its mother particles.

Particle-size Dependency on Disperser Tip Speed

The relation between the particle size and tip speed of the HMS agitator is shown in Table I. The flow rates of both phases were held constant at 3.6 L/h for the monomer phase and 14.4 L/h for the aqueous phase. Increasing the tip speed corresponds to increasing the shear force, which causes the particle size to decrease. Above a tip speed of 35 m/s, the particle size remains relatively constant (see Figure 2). At these tip speeds, the shearing force may be comparable to chemical forces (interfacial tension) in the formation of droplets below 3 microns. Any increase in mechanical force does not contribute to size reduction in small droplets.

Dependence of Feeding Flow Rate on Particle Size

In a typical suspension polymerization process, both the monomer and aqueous phases are charged to the same vessel and mixed to produce the monomer droplets. The phase ratio is an important factor that determines the size of the droplets. In our system proposed in Figure 1, however, the phase ratio can-

Table I Relation between Particle Size and Tip Speed

Tip Speed (m/s)	Av Diameter (Population Base)	Av Diameter (Volume Base)	Mode Diameter
18.0	6.2	9.2	7.8
23.1	3.9	5.5	4.6
30.8	3.3	5.0	3.5
35.9	3.1	4.7	3.1
41.1	3.0	4.4	3.0

Diameters are in microns. Flow rate: monomer, 3.6 L/h; water, 14.4 L/h.

Table II Flow Rate of Monomer and Water Phase

Run	(A) Flow Rate of Monomer Phase	(B) Flow Rate of Water Phase	(A)/(B)
1	6.0	12.0	0.50
2	4.5	13.5	0.33
3	3.6	14.4	0.25
4	3.0	15.0	0.20
5	2.4	15.6	0.15

Flow rate: L/h.

not be determined in the same manner. The ratio of the monomer and aqueous flow rates feeding to the disperser unit can be considered as a factor corresponding to the phase ratio. The experimental flow rates and their ratios are listed in Table II. The particle-size data corresponding to these reaction parameters are presented in Table III. These experiments were conducted at a tip speed of 35 m/s using a 4 : 1 ratio of styrene and *n*-butylacrylate.

Figure 3 shows the particle-size distribution based on the experimental series presented in Table III. The graph clearly displays a sizable effect of flow rate ratios on the particle size and distribution. Figure 4 shows the relation between the mean particle size and the monomer ratio. The monomer ratio is defined as the ratio of monomer divided by the total volume of solution. Figure 4 shows a strong proportional decrease in the particle size upon decrease in the monomer ratio. Unlike the effect of tip speed on particle size, the monomer ratio does not have a tendency to level off. A possible explanation for this difference may be found in the association rate of coalescence. The smaller monomer ratio may give a correspondingly lower association rate.

Table III Effect of Flow Rate on Particle Size

Run	Av Diameter (Population Base)	Av Diameter (Volume Base)	Mode Diameter
1	4.7	6.5	5.1
2	3.6	4.8	3.8
3	3.2	4.7	3.2
4	2.5	3.1	2.5
5	2.2	2.9	2.2

Diameters are in microns. Monomer system : styrene : *n*-butylacrylate = 4 : 1. tip speed = 35 m/s.

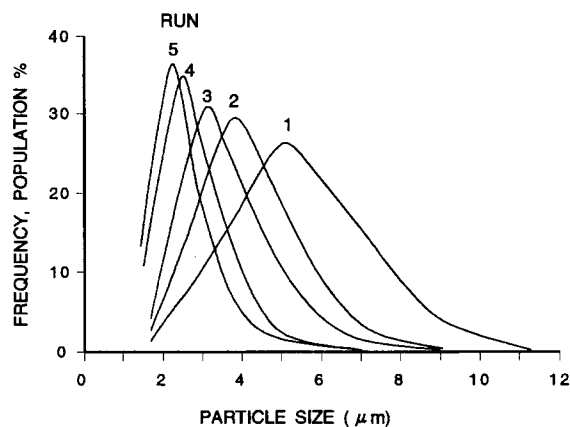


Figure 3 Particle-size distribution. Effect of flow rate ratio. Tip speed = 35.9 m/s. Monomer ratio: (1) 0.50; (2) 0.33; (3) 0.25; (4) 0.20; (5) 0.15.

Relation between Molecular Weight and Particle Size

In the reaction system described above, various sizes of particles are obtained according to the experimental conditions. The relationship between particle size and molecular weight distribution is shown in Figure 5. Also, the relationship of the particle size and average molecular weight is presented in Table IV. These results indicate that there is no appreciable difference in molecular weight distribution among various particle sizes. In suspension polymerization processes, the reaction takes place essentially within each droplet. Each droplet plays the role of an individual reactor.⁹ Generally speaking, the size of the reactor affects the molecular weight and distribution. Therefore, the size of the droplet should affect these polymer properties. However, the results show no relationship between droplet size

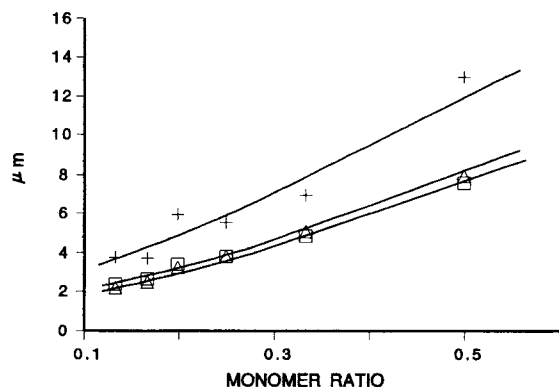


Figure 4 Mean particle size. Effect of monomer ratio: (■) population mean; (+) volume mean; (Δ) mode.

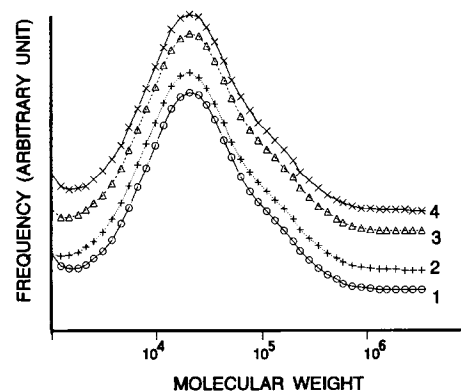


Figure 5 Molecular weight distribution. Effect of particle size. Particle size: (1) 3.4 μm ; (2) 4.0 μm ; (3) 7.0 μm ; (4) 7.3 μm .

and molecular weight. The droplets may be too small to have an effect on molecular weight. Molecular weight can be controlled with the same techniques as applied to conventional suspension polymerization.

Morphological Properties

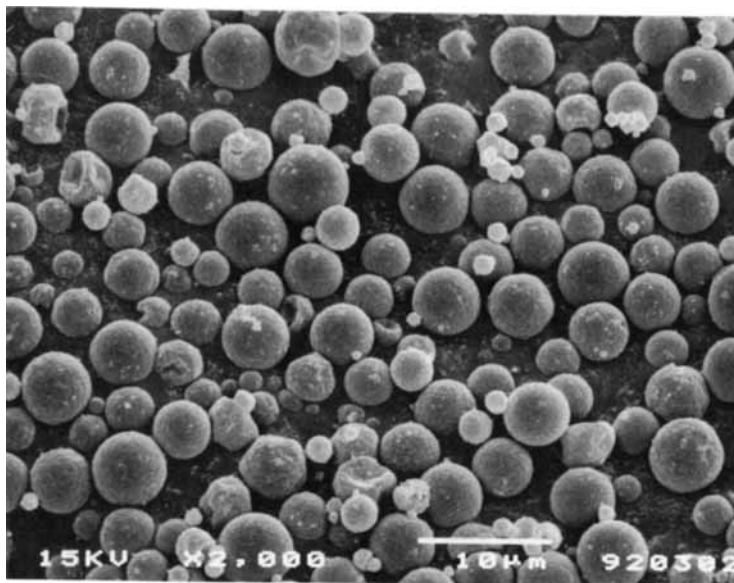
In conventional suspension polymerization processes, the resulting particles typically display irregular structures. These particle irregularities are found at the surface and in the interior of the particles. The morphology of polymer particles has been treated in a number of publications on poly(vinyl chloride). Cebollada and co-workers¹⁰ studied particle morphology for suspension polymerization under various conditions. They suggested that a good relationship exists between polymer conversion and its structure. Davidson and Wintenhafer¹¹ investigated the effect of agitation on the morphology of polymer particles. They stated that when agitation was employed the particle had an irregular internal structure. Both of these reports, however, focus on particles that are tens of microns larger in size and

Table IV Averages of Molecular Weight and Particle Size

Particle Size (Microns)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$
3.4	5.58	1.54
4.0	4.74	1.48
7.0	5.60	1.49
7.3	5.41	1.50

^a Monomer system : styrene : *n*-butylacrylate = 4 : 1.

(A)



(B)

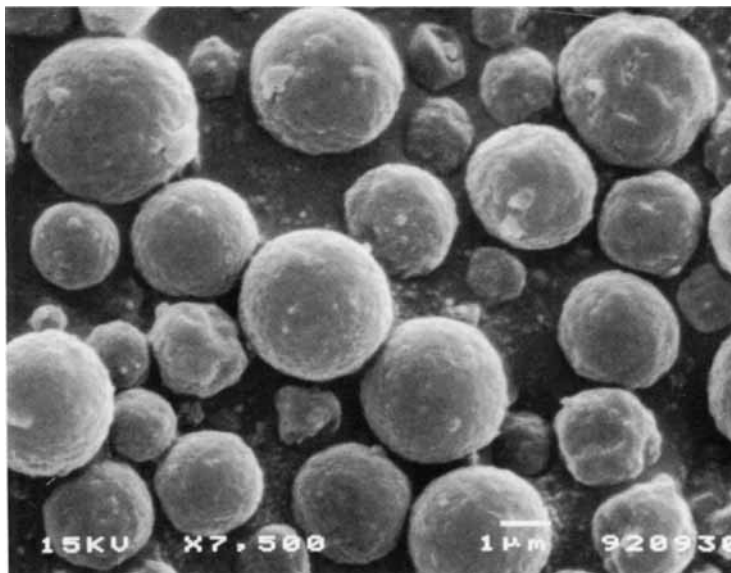


Figure 6 SEM Photographs of Particles: Monomer System (Styrene:n-Butylacrylate = 4 : 1); Tip Speed, 35 m/sec; Particle Diameter (A) $6.5 \mu\text{m}$ ($\times 2000$), (B) $2.9 \mu\text{m}$ ($\times 7500$).

the polymer is insoluble in its monomer. In contrast, the micron-sized particles presented here have a spherical smooth surface (Fig. 6) and have a uniform internal morphology observed by obtaining cross sections of various particles. The particles shown in Figure 6 correspond to experiment 1 (upper pho-

tograph) and experiment 5 (lower photograph) in Table III. It was extremely difficult to obtain irregular-shaped micron-sized particles utilizing the parameters set up with our experimental system. The mechanism for formation of complicated structures typically includes a step of agglomeration of small

particles. These particles are partially colloidally stabilized. The negligible coalescence stage found in our system may avoid the formation of complicated irregular structures.

CONCLUSIONS

Classic polymerization methods for producing polymer particles typically yield either submicron particles (emulsion polymerization) or particles approaching 1 mm in size (suspension polymerization). This work was undertaken to develop a new method for generating particles in the 1–10 micron range. A modified suspension polymerization method was developed during this study. In this method, both the aqueous and monomer phases are fed individually to a high-speed mill where the monomer is uniformly dispersed in the aqueous solution. The system has no limitations on monomers, as long as they are compatible with suspension polymerization processes. The resulting droplets are polymerized in a separate reactor. Particles between 3 and 10 microns were obtained. The size of the particles was controlled by the operating parameters of the system. The particles displayed excellent uniformity and the morphology was spherical in nature with smooth particle surfaces.

REFERENCES

1. J. W. Vanderhoff, J. F. Vitkuske, E. B. Bradford, and T. Alfery, Jr., *J. Polym. Sci.*, **20**, 225 (1956).
2. H. Kawaguchi and Y. Ohtsuka, *Macromol. Chem. Rapid Commun.*, **6**, 315 (1985).
3. C. M. Tseng, Y. Y. Lu, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 2995 (1986).
4. E. Vanzo, *J. Appl. Polym. Sci.*, **16**, 1867 (1972).
5. Y. Almog and M. Levy, *J. Polym. Sci. Polym. Chem.*, **19**, 115 (1981).
6. G. M. H. Lewis and G. Johnson, *J. Vinyl Technol.*, **2**, 102 (1981).
7. Jpn. Pat. H04-004202 (1992).
8. F. H. Winslow and W. Matreyek, *Ind. Eng. Chem.*, **43**, 1108 (1951).
9. G. Talamini and E. Peggion, *Vinyl Polymerization*, Marcel Dekker, New York, 1967, Vol. 1.
10. A. F. Cebollada, M. J. Schmidt, J. N. Farber, N. J. Capiati, and E. M. Valles, *J. Appl. Polym. Sci.*, **37**, 145 (1989).
11. J. A. Davidson and D. E. Witenhafer, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 51 (1980).

Received October 20, 1992

Accepted January 29, 1993