

Polyurethane–Poly(methyl methacrylate) Block Copolymer Dispersions Through Polyurethane Macroiniferters

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ABSTRACT: Polyurethane macroiniferter/poly(methyl methacrylate) block copolymer dispersions with inverse core-shell morphologies were obtained from 1,1,2,2-tetraphenylethane-1,2-diol, dimethylol propionic acid, 4,4'-diphenylmethane diisocyanate, and poly(propylene glycol) via a living radical mechanism. Molecular weight, particle

size and dispersion viscosity, and thermal, mechanical, and dynamic mechanical properties of the dispersion cast films are reported as a function of copolymerization time. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1971–1975, 2003

Key words: polyurethanes; dispersions; ionomers

INTRODUCTION

It is difficult in conventional radical polymerization to control the tacticity, molecular weight, molecular weight distribution, and end groups of polymers because of low chemoselectivity.

The chemoselectivity of a radical polymerization can be improved with living radical polymerization^{1–3} and iniferters.^{4–6} When the propagated polymer radicals are reversibly terminated, polymers with well-controlled structures are obtained. The concepts of iniferter and living radical polymerization have successfully been used to prepare homopolymers,⁷ block copolymers,⁸ and ionomers⁹ through polyurethane macroiniferters (PUMIs).¹⁰

In a past study,¹¹ we modified polyurethane anionomer (PUA) dispersions to improve solvent and water resistance by incorporating various types of acrylate monomers via a latex AB-crosslinked polymer technique.

In this work, a PUMI dispersion was obtained with 1,1,2,2-tetraphenylethane-1,2-diol (TPED), ionic chain extender, polyol, and isocyanate, and PUMI–poly(methyl methacrylate) (PMMA) block copolymer dispersions were obtained with latex core-shell morphologies through the living radical polymerization of methyl methacrylate (MMA). In addition, *in situ* polymerizations of MMA in the presence of the PUA dispersion, which were extended by ethylene glycol (EG) instead of TPED in PUMI, were also prepared

within the PUA particles. Subsequently, an inverse core (PMMA)-shell (PUMI or PUA) morphology was created, and the mechanical and dynamic mechanical properties of the two types of dispersion cast films compared favorably in terms of polymer structure.

Experimental

Materials

MMA (TCI, Tokyo, Japan) was distilled at a reduced pressure, and the middle portion was stored at 0–4°C until use. Poly(propylene glycol) (Aldrich, Milwaukee, WI) with a molecular weight of 1000 (PPG-1000) was dried under vacuum at 105°C before use. 4,4'-Diphenylmethane diisocyanate (MDI) was melted at 60°C, filtered with a hot funnel, and stored at 0–4°C until use. Dibutyltindilaurate (DBTDL) was used as received from Aldrich. Dimethylformamide (DMF) was distilled, and the middle portion was stored over a molecular sieve (4 Å) until use. TPED was prepared from 2-propanol and benzophenone.¹² All other chemicals were used as received. The formulations are given in Table I.

Characterizations

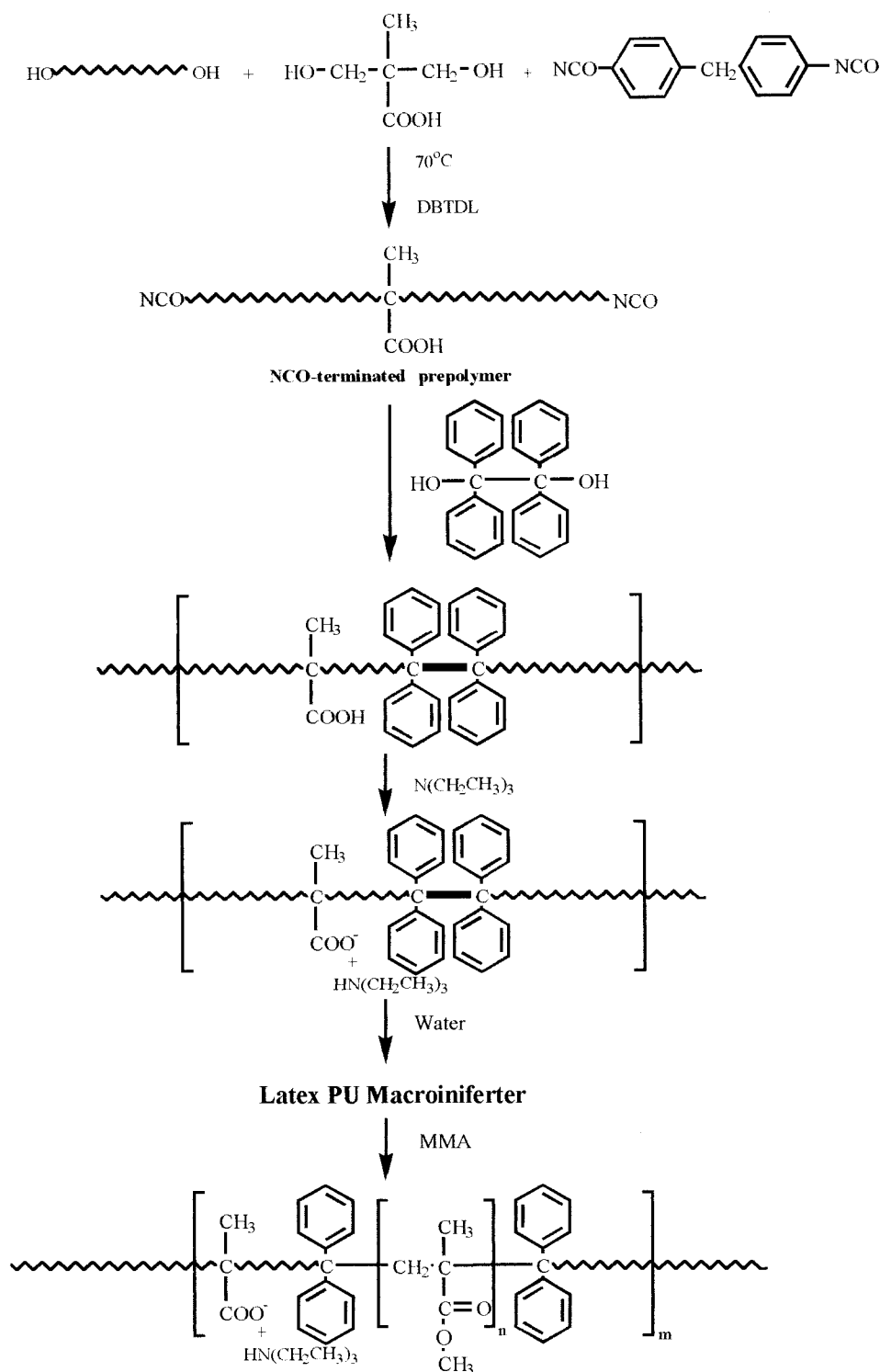
A gel permeation chromatograph (GPC Waters, Milford, MA), equipped with four ultra styragel columns and a refractive index (RI) detector, was used to determine the average molecular weight and its distribution. High performance liquid chromatography (HPLC)-grade DMF (0.01% LiBr added) was used as an effluent at a flow rate of 1.0 mL/min, and polystyrene standards were used to calibrate the molecular

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weights. For gel permeation chromatography measurements, PUMI and PMMA homopolymers were extracted with acetone and ethyl ether, respectively. Particle size and distribution were determined with an autosizer (Malvern IIC, London, UK). Tensile properties were studied with a Tinius Olsen (Horsham, PA) tensile tester at a crosshead speed of 100 mm/min.

Tensile specimens were prepared according to the method in ASTM D 142. Dynamic mechanical properties were measured with a Rheovibron (Orientec DDV 01-FP) (Tokyo, Japan) at 11 Hz for a sample size of $0.03 \times 0.2 \times 3$ cm. Differential scanning calorimetry (DSC) measurements were carried out on a DuPont MDSC 2010 (Wilmington, DE) at a heating rate of $10^\circ\text{C}/\text{min}$.



Scheme 1 Process of latex PUMI-PMMA multiblock copolymer.

TABLE I
Formulation and GPC Data of PUMI/PMMA Block Copolymers

PUMI		MMA		Polymerization time (h)	Yield (%)	GPC results	
Weight (g)	wt %	Weight (g)	wt %			M_n	M_w/M_n
6	60	4	40	0	0	4.82	2.82
6	60	4	40	3	14.2	5.43	2.65
6	60	4	40	6	27.8	6.15	2.52
6	60	4	40	12	51.1	7.3	2.35
6	60	4	40	24	94.5	9.26	2.15

Synthesis (Scheme 1)

The procedures we used to prepare PUA and PUMI dispersions are well documented in our earlier works.¹³⁻¹⁸

MDI (3 mol), dimethylol propionic acid (1 mol), and PPG-1000 (1 mol) were reacted for over 1 h at 70°C to obtain the NCO-terminated prepolymer. To this, 1 mol of TPED and DBTDL (0.03 wt % based on PUMI) were added and stirred for 24 h at 30°C. Solid content was kept at about 50% with DMF; then, the resulting solution was neutralized by the addition of 1 mol of triethylamine as neutralizing agent at 60°C for 1 h. Then, the solution was cooled to 25°C, and water was subsequently added dropwise with a tubing pump at constant flow rate to make latex PUMI. The speed of agitation was kept at 1000 rpm. Block copolymerization of MMA on PUMI was done via a living radical mechanism. MMA was added to the PUMI dispersion and polymerized for 24 h (40 wt % of PUMI). PUA dispersions were prepared by extension of the NCO terminated prepolymers with EG, instead of TPED in PUMI. So, PUA/PMMA (6/4) was *in situ* polymerized in the presence of PUA with potassium persulfate as a water-soluble initiator. The latex PUMI was precipitated in a 10-fold excess of methanol. GPC results of PUMI are as follows:

$$M_n = 4.8248 \times 10^4; M_w = 13,600 \times 10^4; M_w/M_n = 2.82$$

number-average molecular weight (M_n) = 4.8248×10^4 , weight-average molecular weight (M_w) = $13,600 \times 10^4$, and $M_w/M_n = 2.82$.

RESULTS AND DISCUSSION

The synthetic route used to prepare the dispersions is given in Scheme 1. GPC results of block copolymerizations, as a function of reaction time, are given in Table I. As the polymerization time increased, the conversion of MMA into block copolymer, namely, the yield, increased. A linear plot between yield and M_n (Fig. 1) showed that the formation of block copolymers was through a living radical mechanism.

Figure 2 shows the effect of polymerization time on the particle size of the PUMI/MMA (6/4) dispersions. The particle size increased and viscosity decreased with increasing polymerization time. The increase of particle size was due to the diffusion of MMA molecules into droplets. However, the viscosity decrease was most likely due to the increased hydrophobicity of particles by MMA incorporation.

Figure 3 shows the dynamic mechanical properties of cast films of PUMI, PUA, the PUMI-PMMA (6/4) block copolymer dispersion, and the *in situ* polymer-

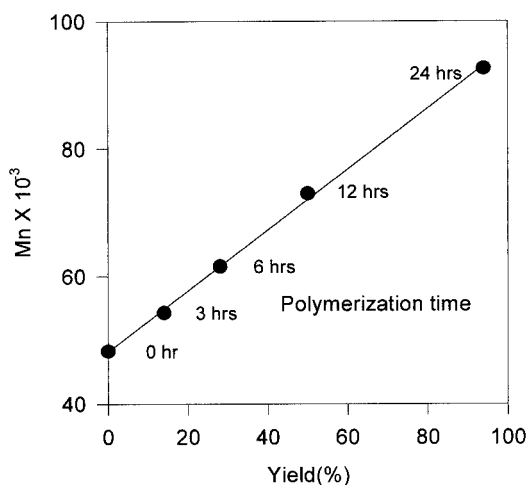


Figure 1 Polymerization time-yield- M_n relationship for PUMI-PMMA block copolymerization (PUMI-PMMA = 6/4 w/w).

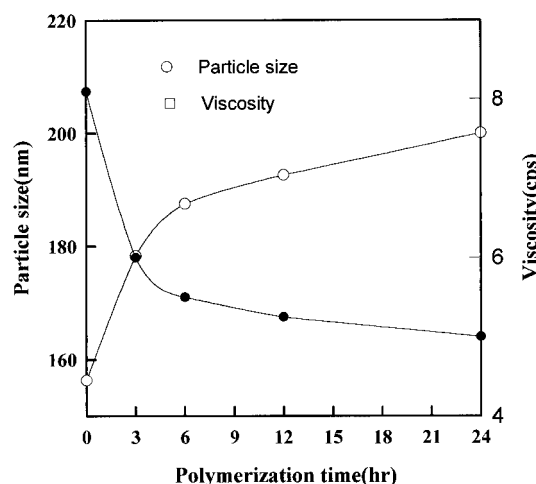


Figure 2 Effect of polymerization time on the particle size and viscosity of PUMI-PMMA block copolymer dispersion.

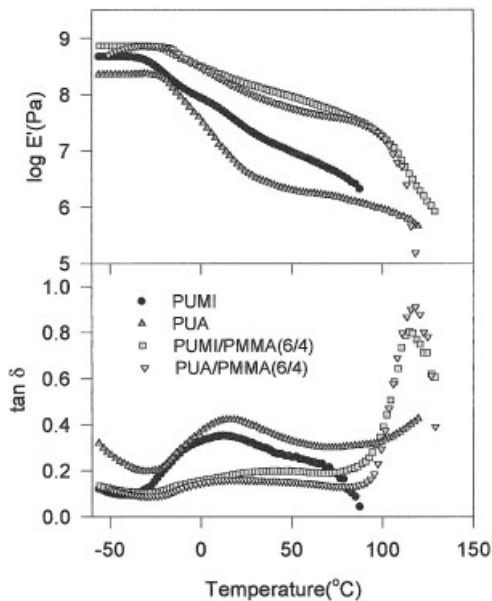


Figure 3 Storage modulus and $\tan \delta$ of PUMI, PUA, PUMI-PMMA (6/4) copolymer, and PUA/PMMA (6/4) IPN dispersions (reaction time = 24 h).

ized PUA/PMMA (6/4) dispersion. The storage moduli of PUMI and PUMI-PMMA block copolymer were, respectively, greater than those of PUA and the *in situ* blend of PUA/PMMA, due mainly to the greater chain rigidity of TPED as compared with EG. Dampening of PUA and interpenetrating polymer network (IPN) in terms of a $\tan \delta$ peak were well defined compared with PUMI and the copolymer, implying that the extent of phase separation was greater with PUA and IPN. Both in the block copolymer and IPN, the glass-transition temperature (T_g) of the PU block was a mere shoulder, whereas that of PMMA was a sharp peak.

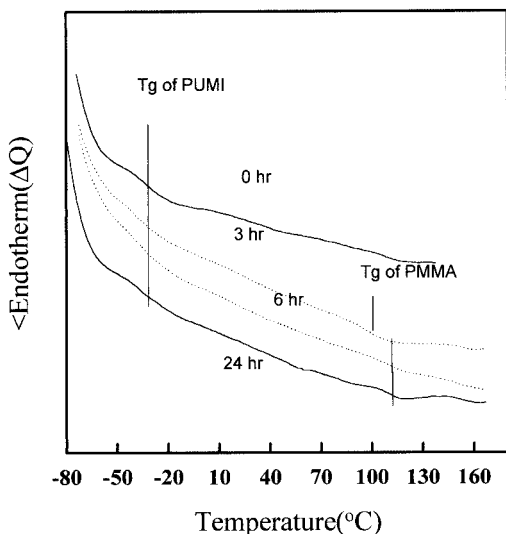


Figure 4 DSC thermograms of PUMI-PMMA block copolymers prepared at various reaction times.

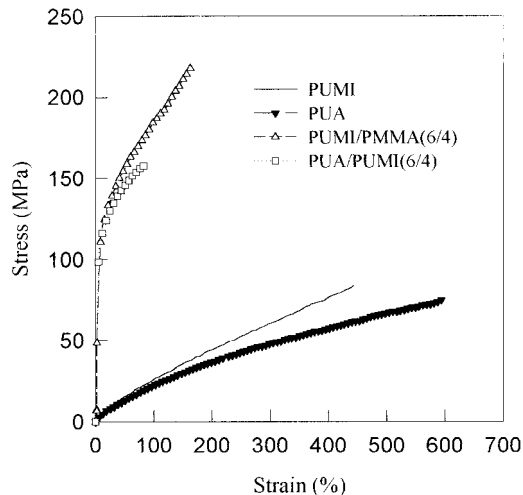


Figure 5 Stress and strain curves of PUMI, PUA, PUMI-PMMA (6/4) copolymer, and PUA/PMMA (6/4) IPN (reaction time = 24 h).

Figure 4 shows the DSC thermograms of the PUMI-PMMA block copolymer dispersion cast films that were obtained as a function of PMMA polymerization time. The glass-transition behavior of PUMI was not changed and became insignificant with the progress of the reaction. However, the T_g of the PMMA block increased with polymerization reaction because of the increased PU/PMMA phase separation.

Figure 5 shows the tensile behavior of the cast films of PUMI, PUA, the PUMI-PMMA (6/4) copolymer dispersion, and the *in situ* polymerized PUA/PMMA (6/4) blend. PUMI showed a somewhat higher initial modulus consistent with dynamic mechanical measurements and a lower elongation at break as compared with PUA.

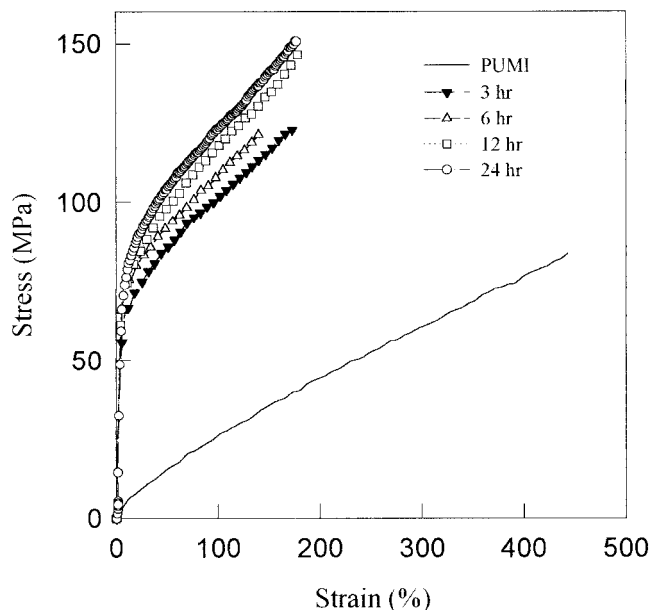


Figure 6 Stress-strain curves of PUMI-PMMA copolymer dispersion cast films versus reaction time.

Lower ductility and more likely linear elastic behavior of PUMI were probably due to its rigidity and the brittle nature of the TPED segment. However, the block copolymer showed a much greater strength and toughness compared with IPNs. This should be an advantage for the block copolymer over the blends.

Figure 6 shows the tensile behaviors of PUMI-PMMA copolymer dispersion cast films that were obtained as a function of polymerization time. Initial modulus and tensile strength increased with increasing polymerization time because of the incorporation of the PMMA block. Continuous growth of strength with reaction time was due to the increased molecular weight, implying that the reaction proceeded via a living mechanism.

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