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SHORT COMMUNICATION

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Polyurethane-polymethacrylic acid multiblock copolymer dispersions through polyurethane macroiniferters

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Abstract Polyurethane-polymethacrylic acid multiblock copolymers have been prepared from tetraphenylethane-based polyurethane macroiniferters. Aqueous dispersions of these block copolymers and their anionomers have been prepared. Anionomeric dispersions have smaller particle size and higher viscosity when compared to their corresponding block copolymeric dispersions. Particle size decreases whereas viscosity increases when the degree of neutralization is increased. Tensile strength and initial modulus are higher for films derived from anionomeric dispersions than for the corresponding block copolymeric films.

Key words Polyurethane dispersions – Macroiniferters – Iniferters – Living radical polymerization – Multiblock copolymers

Introduction

Block copolymers play a vital role in polymer industries due to their microphase separated morphology. They are used as compatibilizing agents for immiscible blends [1, 2], thermoplastic elastomers [3], adhesives [4], coating materials [5] and surfactants. Ethylene oxide-*b*-propylene oxide is the most widely used block copolymeric surfactant in the chemical and pharmaceutical industries [6, 7]. This type of block copolymer behaves like typical hydrophobic-hydrophilic agents and its surface activity mainly depends on the block length of the hydrophilic and hydrophobic segments. Since the block lengths can easily be altered through iniferter and "living" radical polymerizations, different types of hydrophilic-hydrophobic block copolymers have been synthesized using polyurethane macroiniferters (PUMI) through "living" radical polymerization [8–11].

Iniferters and macroiniferters

An iniferter is an initiator, transfer agent and/or terminator in radical polymerization [12]. Dithiocarbamate [13], thiuram disulfide [14] and tetraphenylene derivatives are the major iniferters which have been widely studied. Recently, free radical polymerization by mediated nitroxide-stable free radicals such as 2,2,6,6-tetramethyl-1-piperidinyl-1-oxy or 4-methoxy-2,2,6,6-tetramethyl-piperidine-1-oxy were reported to yield polymers with narrow polydispersities [15–18], or block copolymers quantitatively [19]. Primary radical termination predominantly occurs in iniferter polymerization which leads to the control over molecular weight and end groups of the resulting polymer. Polymers which consist of iniferter groups can be introduced in macroiniferters

1. At one end of each polymer chains.
2. At both ends of each polymer chain.
3. Between polymer blocks.
4. As side chains.
5. Between organic groups such as urethane, amide, ester, etc.

When these types viz. 1–5 are decomposed in the presence of vinyl monomers, diblock, triblock, multiblock, graft copolymers and homopolymers are obtained, respectively. Tetraphenylethane [8–11, 20], dithio carbamate [21, 22] and thiuram disulfide [23] derivatives are the widely studied macroiniferters.

"Living" radical polymerization

Living radical polymerization is a radical polymerization without irreversible termination and transfer reactions [24]; however irreversible termination and transfer reactions cannot be avoided fully in radical polymerization. When irreversible termination and transfer reactions in radical polymerization are below the detection limit using currently available instruments, the polymerization "living" or controlled radical polymerization [24]. "Living" radical polymerization can be achieved through reversible deactivation of propagating species. Reversible deactivation through iniferters [8–14], persistent radicals [25] and degenerative transfer agents [26] are the three ways to achieve "living" radical polymerization. The mechanism of "living" radical polymerization through iniferters is given in Eq. (1).

$$\begin{aligned} &\underset{(A)}{P_n\text{—}I} \rightleftharpoons \underset{(B)}{P_n\bullet} + \underset{(C)}{I\bullet} \xrightarrow{xP} \underset{(D)}{P_{n+x}\text{—}I} \\ &(D) \rightleftharpoons P_{n+x}\bullet + I\bullet \xrightarrow{yP} P_{n+x+y}\text{—}I \longrightarrow \end{aligned} \tag{1}$$

Here P_n—I is a polymer/oligomer obtained from the reversible deactivation between propagated radical, $P_n\bullet$, and iniferter scavenging radical, I•. The scavenger, I• can only react with $P_n\bullet$ but not with monomer (P) molecules.

As described above, PUMI can be used to synthesize PU-based block copolymers with hydrophilic segments. It is well known that hydrophobic-hydrophilic block copolymers can form aqueous dispersions if proper reaction conditions are employed. In this paper, studies on the preparation of PU-polymethacrylic acid (PU-PMA) multiblock copolymeric dispersions are presented.

Experimental

Materials

Methacrylic acid (TCI, Japan; MA) was distilled at reduced pressure and the middle portions were stored at 0–4 °C until use. Poly(tetramethyleneoxide) glycol (Aldrich, USA) of molecular weight 1000 (PTMG-1000) was dried under vacuum at 105 °C prior to use. Diphenylmethanediisocyanate (MDI) was melted at 60 °C, filtered using hot funnel and stored at 0–4 °C until use. Dibutyltindilaurate (DBTDL) was used as received from Aldrich. Methylethylketone (MEK) and dimethylformamide (DMF) were distilled and the middle portions were stored over molecular sieves (4 Å) until use. 1,1,2,2-Tetraphenylethane-1,2-diol (TPED) was prepared from 2-propanol and benzophenone [27]. All other chemicals were used as received.

Characterization techniques

A gel permeation chromatograph (GPC) (Waters) equipped with four ultra styragel columns and a RI detector was used to determine the average molecular weight and distribution. 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 molecular weights. For GPC measurements, PUs and PMA homopolymers were extracted using acetone and distilled water, respectively [8]. Particle size and distribution were determined using an Autosizer (Malvern IIC). Viscosity measurements were carried out using a Brookfield viscometer at 20 °C. Mechanical properties were studied using a tensile tester (Tinius Olsen 1000) at a crosshead speed of 100 mm/min. Tensile specimens were prepared according to the ASTM D-142 method. Dynamic mechanical properties were measured using a Rheovibron (Orientec DDV 01-FP) at 11 Hz for a sample size of 0.03 × 0.2 × 3 cm.

Synthesis of PUMI

MDI (75 g, 0.3 M) and PTMG-1000 (150 g, 0.15 M) were reacted at 60 °C to obtain NCO-terminated prepolymer. To this, 54.969 g (0.15 M) TPED, 3.7894 g (2 mol % based on initial MDI) DBTDL and 567 ml MEK were added and stirred for 24 h at 30 °C. The resulting PUMI was precipitated in tenfold excess of methanol. The GPC results of PUMI are given below.

$$M_n = 4.6384 \times 10^4; M_w = 8.4419 \times 10^4; M_w/M_n = 1.82$$

Synthesis of PU-PMA multiblock copolymers and their anionomers

Required amounts of PUMI, DMF and MA (Table 1) were put in a cylindrical Pyrex tube and polymerized after degassing at 75 °C. After the desired reaction time, the reactions were stopped by dipping the tube in an ice-salt mixture. Calculated amounts of triethylamine were added to the block copolymeric solutions and kept at 25 °C overnight to prepare block copolymeric anionomers. Yield and GPC results of block copolymers are given in Table 1. The detailed procedures to prepare PUMI and PU-PMA multiblock copolymers were reported elsewhere [11].

Preparation of dispersions

Block copolymer of anionomer (6 g) was dissolved in 24 ml DMF at 25 °C. This solution was homogenized by stirring at 50 °C for 15 min. Then it was cooled to 25 °C and 55.7 ml water was subsequently added dropwise using a tubing pump with constant flow rate. The speed of agitation was kept at 1000 rpm. One part of the resulting dispersion was put onto a Teflon plate and dried at 50 °C to obtain a film. This film was stored at 25 °C for 48 h in vacuum before characterization.

Results and discussion

Several anionomeric and cationomeric PU dispersions have been prepared successfully in our laboratory [28–31]. As a continuation of our research on dispersions, studies on PU-PMA multiblock copolymeric dispersions are reported in this paper. The synthetic route used to prepare dispersions is given in Scheme 1. Basic formulations of block copolymers and their anionomers are given in Table 1, together with yield and GPC results of block copolymers. As the feed ratio of PUMI decreases, the yield of the block copolymers also

Table 1 Synthesis and characterization of polyurethane (*PU*)-polymethacrylic acid (*PMA*) multiblock copolymers and their anionomer[a]

PUMI		MA		Time (h)	Triethylamine		Yield[b] (%)	GPC results	
Wt (g)	Wt (%)	Wt (g)	Wt (%)		Wt (g)	Percentage of neutralization		$M_n \times 10^{-4}$	M_w/M_n
9	90	1	10	12	–	–	84.02	5.27	2.15
9	90	1	10	12	1.18	100	–	–	–
8	80	2	20	12	–	–	64.85	5.62	2.23
8	80	2	20	12	2.35	100	–	–	–
7	70	3	30	12	–	–	57.86	6.21	2.25
7	70	3	30	12	3.53	100	–	–	–
6	60	4	40	12	–	–	64.07	6.82	2.43
6	60	4	40	12	4.70	100	–	–	–
5	50	5	50	12	–	–	59.72	7.25	2.59
5	50	5	50	12	5.88	100	–	–	–
4	40	6	60	12	–	–	59.38	7.62	2.75
4	40	6	60	12	7.05	100	–	–	–
3	30	7	70	12	–	–	62.32	8.52	2.85
3	30	7	70	12	8.22	100	–	–	–
2	20	8	80	12	–	–	47.30	10.75	3.26
2	20	8	80	12	9.40	100	–	–	–
6	60	4	40	3	–	–	30.53	5.20	2.31
6	60	4	40	3	4.70	100	–	–	–
6	60	4	40	6	–	–	46.18	5.82	2.53
6	60	4	40	6	4.70	100	–	–	–
6	60	4	40	24	–	–	98.55	8.14	2.12
6	60	4	40	24	4.70	100	–	–	–
6	60	4	40	12	1.17	25	–	–	–
6	60	4	40	12	2.35	50	–	–	–
6	60	4	40	12	3.52	75	–	–	–

[a] Dimethyl Formamide = 52.5 ml

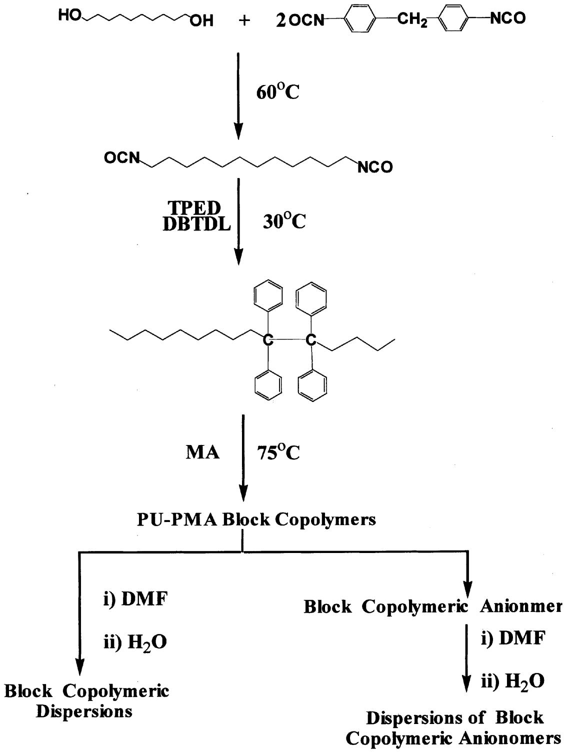
[b] $\text{Yield} = \frac{\text{copolymerized MA}}{\text{MA in feed}}$

decreases. As the PUMI feed ratio decreases, the number of initiation species also decreases and hence the yield also decreases. As the PUMI feed ratio decreases, the feed ratio of MA increases. The increased amount of MA increases the incorporation of MA units into the block copolymers. Hence, as the feed ratio of PUMI decreases, the molecular weight of the block copolymer increases. As already reported [8–12, 25, 26], as polymerization time increases, conversion of MA into the block copolymer viz. yield increases. A linear plot of yield and M_n (Fig. 1) shows that the formation of block copolymers is through the "living" radical mechanism.

Block copolymers prepared from 90–70% PUMI do not have enough hydrophilic segments (PMA blocks) to form stable dispersions. Hence only block copolymers prepared from 60% PUMI and below are able to form stable dispersions. However, block copolymeric anionomers from a 70% PUMI feed ratio and below are able to form stable dispersions, since block copolymeric anionomers are more hydrophilic than their corresponding block copolymers.

The effect of PUMI content on particle size and viscosity of the dispersions is shown in Fig. 2. It seems that viscosity increases and particle size decreases with increasing PUMI content. In general, viscosity increases as particle size decreases due to the larger hydrodynamic volume of the smaller particles. The simultaneous decrease of particle size and viscosity implies of that PUMI contributes to the size reduction in one way and to the viscosity decrease another. That is, with more PUMI, particle size decreases due to the decreased molecular weight and hence the viscosity of the polymer phase, leading to easier breakup during dispersion in water. On the other hand, the PUMI block is more hydrophobic than the PMA block, and hence decreases the viscosity. It seems that the latter effect viz. hydrophobicity dominates in our case. It is noted that anionomer results in smaller particle size, greater viscosity and the block copolymer due to the fact that the hydrophilicity of the block copolymers increases when the COOH groups are converted into carboxylate anionomers.

The effect of polymerization time on viscosity and particle size of the dispersions is shown in Fig. 3. As polymerization time increases molecular weight increases leading to an increase in particle size and hence dispersion viscosity due to the increased molecular weight and solid fraction. Anionomeric dispersions have



Scheme 1

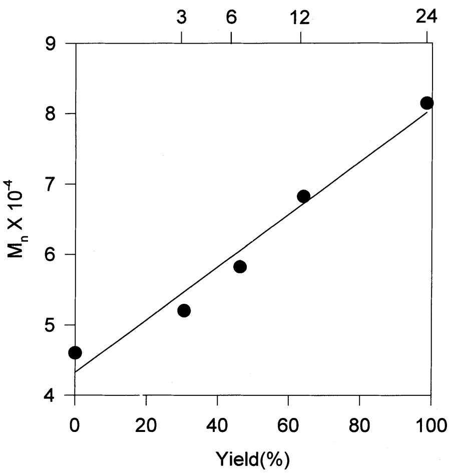


Fig. 1 Polymerization time-copolymer yield-M_n relationship for polyurethane (*PU*)-polymethacrylic acid (*PMA*) multiblock copolymerization [PU macronifeters (*PUMI*)/methacrylic acid = 6/4 by weight]

smaller particle size and higher viscosity when compared to their corresponding block copolymers as illustrated in Fig. 2. At constant solid content smaller particles produce larger hydrodynamic volumes and hence greater dispersion viscosity.

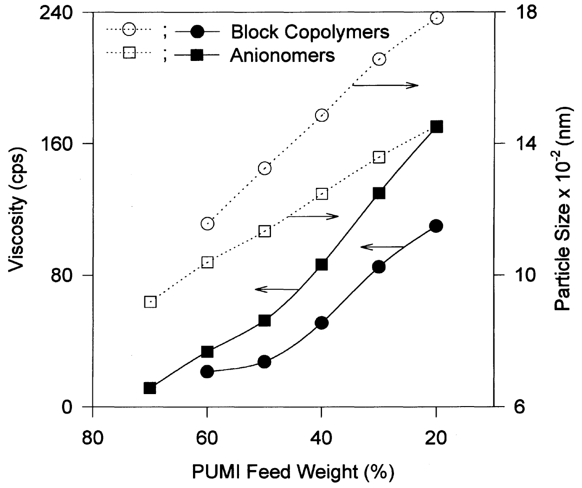


Fig. 2 Effect of PUMI feed ratio on viscosity and particle size of PU-PMA multiblock copolymer and their anionomer dispersions

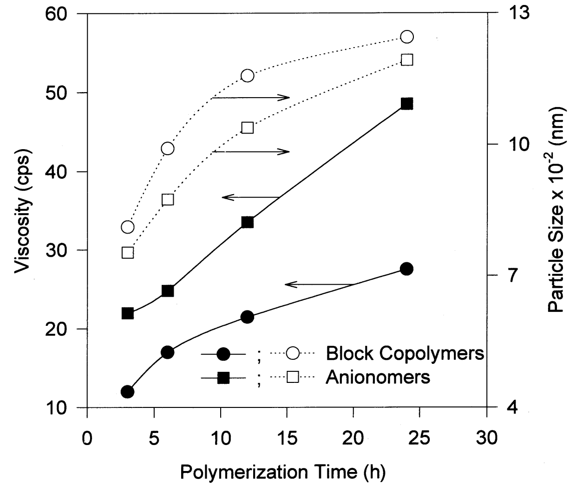


Fig. 3 Effect of time on viscosity and particle size of dispersions of PU-PMA multiblock copolymer and their anionomer dispersions

The effect of the degree of neutralization on viscosity and particle size of the dispersions is shown in Fig. 4. As the degree of neutralization is increased, hydrophilicity increases leading to decreased particle size and increased viscosity.

Figure 5 shows the effect of PUMI feed ratio on tensile properties of the films obtained from the dispersions. As the PUMI feed ratio decreases, there is a decrease in both tensile strength and elongation at break. As the PUMI feed ratio is decreased, the percentage of PMA in the block copolymer increases. Since PMA is brittle, as the percentage of the PMA block increases, the films become brittle and hence both tensile strength and elongation at break decrease.

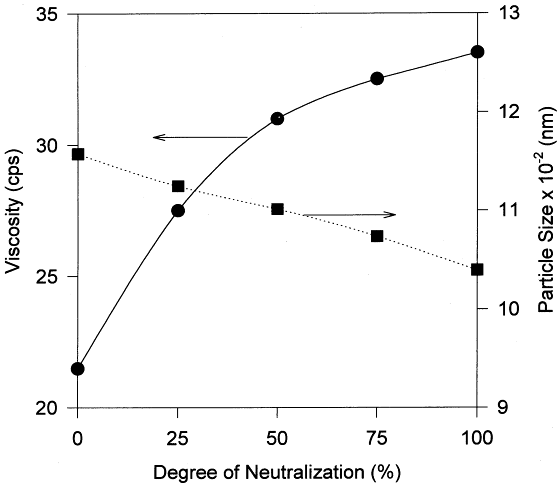


Fig. 4 Effect of degree of neutralization on viscosity and particle size of PU-PMA multiblock copolymer and their anionomer dispersions

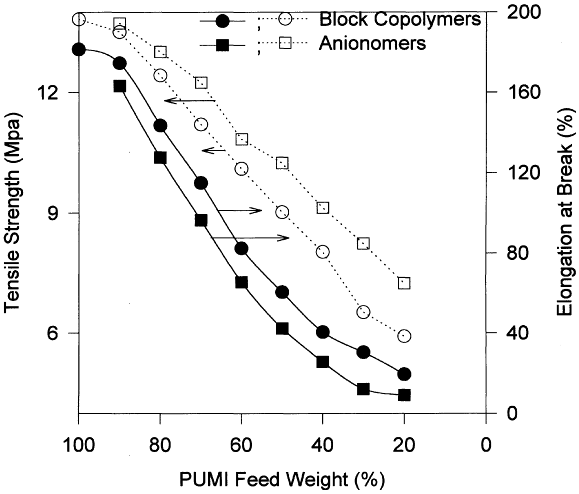


Fig. 5 Effect of PUMI feed ratio on tensile behavior of the films derived from PU-PMA multiblock copolymer and their anionomer dispersions

Tensile strength increases and elongation at break decreases when the block copolymers are converted into anionmers as reported already [32]. The effect of PUMI feed ratio and degree of neutralization on the initial modulus of the films is shown in Fig. 6. As the PUMI feed ratio decreases, PMA incorporation into the block copolymers increases and thereby the initial modulus of the films also increases. Anionomeric films have higher initial moduli that their corresponding block copolymers.

The effect of the degree of neutralization on tensile strength and elongation at break of the films is shown in Fig. 7. As the degree of neutralization increases, tensile strength also increases but elongation at break decreases as illustrated in Fig. 5.

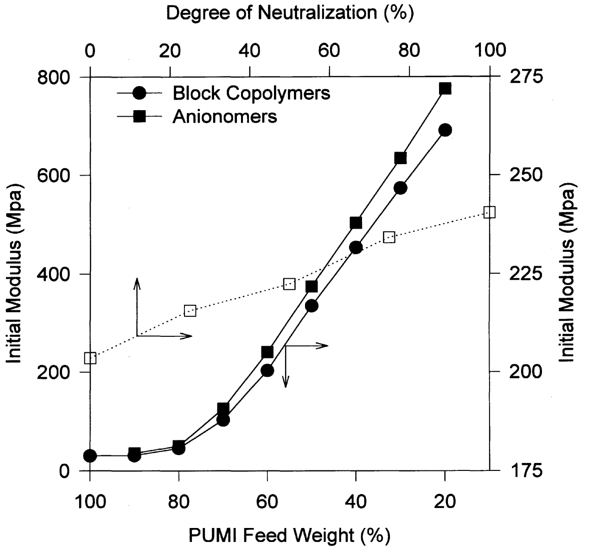


Fig. 6 Effect of PUMI feed ratio and degree of neutralization on initial modulus of the films derived from PU-PMA multiblock copolymer and their anionomer dispersions

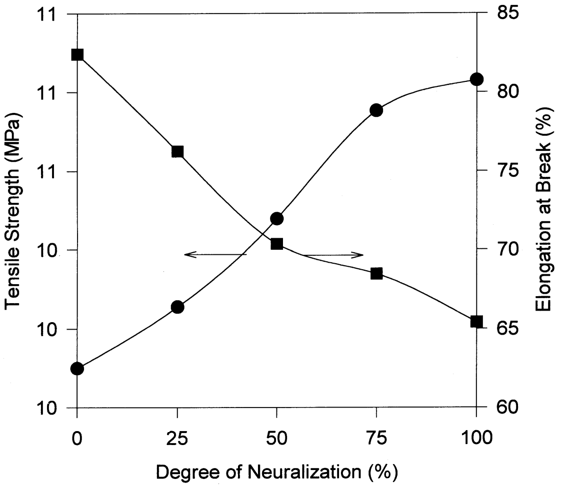


Fig. 7 Effect of degree of neutralization on tensile behavior of the films derived from PU-PMA multiblock copolymer and their anionomer dispersions.

Figure 8 shows the effect of polymerization time on tensile strength and elongation at break of the films obtained from the dispersions. As polymerization time decreases, incorporation of the brittle PMA block also increases which results in both tensile strength and elongation at break decreasing. As in the case illustrated in Fig. 4, the anionomers have higher tensile strength and lower elongation at break when compared to their corresponding block copolymers.

Figure 9 shows tan δ versus temperature curves obtained from dynamic mechanical studies of the films

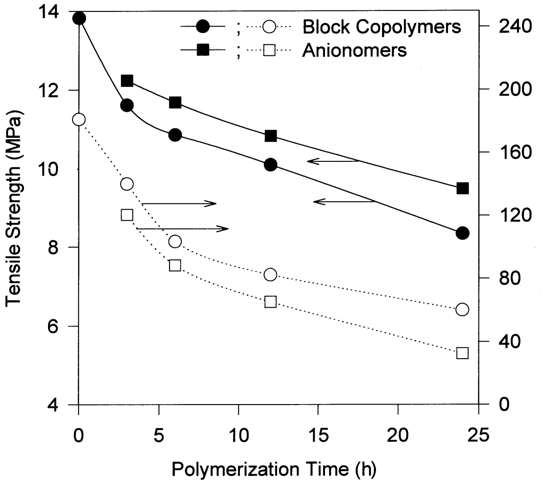


Fig. 8 Effect of polymerization time on tensile behavior of the films derived from PU-PMA multiblock copolymer and their anionomer dispersions

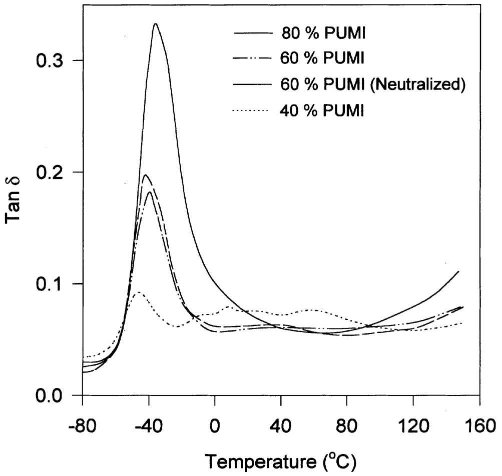


Fig. 9 Temperature-tan δ curves of the films derived from PU-PMA multiblock copolymer dispersions

obtained from PU-PMA multiblock copolymeric dispersions. As the PUMI feed ratio decreases, T_g of the soft block also decreases from −35.8 °C (from 80% PUMI) to −46.1 °C (from 40% PUMI). As the PUMI feed ratio decreases, PMA block length increases. The increase in block length augments the degree of phase separation which increases phase purity, and thereby T_g of the soft block decreases. When COOH groups are converted into anionomers the same effect occurred and hence block copolymer, prepared from 60% PUMI, has a higher T_g (−40.7 °C) than its corresponding anionomer (T_g = −42 °C).

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