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Multi-block copolymer dispersions through polyurethane macroiniferters

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Summary

Tetraphenylethane-based polyurethane macroiniferter has been used to prepare polyurethane-polymethacrylic acid multi-block copolymers. These block copolymers have been converted into corresponding anionomers by treating them with triethylamine. Dispersions have been prepared by adding water into dimethylformamide solutions of block copolymers and their anionomers. Particle size and viscosity of the dispersions have been determined. The films obtained from the dispersions have been characterized by mechanical and dynamic mechanical analyses.

Introduction

Block copolymers show interesting colloidal and interfacial properties analogous to surface active agents. When a block copolymer is dissolved in a selective solvent, in which one of the block is soluble and the other block is insoluble, it can form micelles (1). These type of micelles have been used in stabilizing colloidal dispersions (2), solubilization of insoluble substances (3) etc. Block copolymer consisting of hydrophilic blocks linked to hydrophobic blocks can form micelles (4) if water is used as a selective solvent. These type of block copolymers are used in water-oil emulsions (5). Due to the strict environmental regulations, aqueous polymeric systems are being encouraged in coating industries. Several anionic and cationic polyurethane (PU) dispersions have been prepared in our laboratory (6-8).

Iniferter is an initiator, transfer agent and/or terminator in radical polymerization (9). Tetraphenylethane-based PU macroiniferters have been synthesized and used to prepare multi-block copolymers through “living” radical mechanism (10-12). In continuation of our research on dispersions, preparation and properties of PU-polymethacrylic acid (PU-PMAA) multi-block copolymeric dispersions through PU macroiniferter are reported in this paper.

Experimental

Materials

Poly(tetramethyleneoxide) glycol (Aldrich, USA) of molecular weight 2000 (PTMG-2000) was dried under vacuum at 105°C and used. Diphenylmethanediisocyanate (MDI) was heated at 60°C, filtered using hot funnel and used. Dibutyltindilaurate (DBTDL) was used as received from Aldrich, USA. Distillation of methacrylic acid (TCI, Japan; MAA) was carried out at reduced pressure and the middle portions were stored at 0-4°C until use. Methylethylketone (MEK) and dimethylformamide (DMF) were distilled and the middle portions were stored over molecular sieves (4Å) until use. 1,1,2,2-Tetraphenylethane-1,2-diol (TPED) was prepared from 2-propanol and benzophenone using glacial acetic acid as a sensitizer (13).

Characterization techniques

Gel permeation chromatography (GPC) (Waters) attached 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. Polystyrene standards were used to calibrate molecular weights. Viscosity measurements were carried out using Brookfield viscometer at 20°C. Particle size and distribution were determined using Autosizer (Malvern IIC). Mechanical properties were studied using tensile tester (Tinius Olsen 1000) at a crosshead speed of 100 mm/min. ASTM D-142 was used to prepare tensile specimens and an average of five values were considered to report one value. Dynamic mechanical properties were measured using an Orientec DDV 01-FP rheovibron at 11Hz for a sample size of 0.03 X 0.2 X 3cm.

Synthesis of PU-PAMAA multi-block copolymers and their anionomers

PU macroiniferter (PUMI) was synthesized as follows. 10 g (0.04 mole) of MDI and 40 g (0.02 mole) of PTMG-2000 were reacted at 60°C to obtain NCO terminated prepolymer. To this, 7.3292 g (0.02 mole) of TPED, 0.5053 g (2 mole % based on initial MDI taken) and 116 ml of MEK were added and stirred for 24 hrs at 30°C. The resulting PUMI was precipitated in 10 fold excess of methanol. GPC results of PUMI are given below.

$M_n=8.0345\text{x}10^4$; $M_w=14.7272\text{x}10^4$; $M_w/M_n=1.83$

PU-PMAA multi-block copolymers and their anionomers were synthesized as follows. Required amounts of PUMI, DMF and MAA (cf. Table 1) were taken in a cylindrical Pyrex tube and polymerized after degassing at 75°C. After 12 hrs, the reactions were arrested by dipping in a ice-salt mixture. Calculated amounts of triethylamine was 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 procedure to prepare PUMI and PU-

Table 1. Synthesis and characterization of PU-PMAA multi-block copolymers and their anionomers

PUMI		MAA		DMF (ml)	Triethylamine		Yield (%)	GPC results	
Wt (g)	Wt (%)	Wt (g)	Wt (%)		Wt (g)	% of neutralization		Mn x 10^{-4}	Mw/Mn
8	80	2	20	52.5	-	-	90.08	8.97	2.45
8	80	2	20	52.5	2.35	100	-	-	-
6	60	4	40	52.5	-	-	74.26	10.44	2.31
6	60	4	40	52.5	4.70	100	-	-	-
4	40	6	60	52.5	-	-	59.15	11.91	2.29
4	40	6	60	52.5	7.05	100	-	-	-
2	20	8	80	52.5	-	-	51.93	21.81	1.78
2	20	8	80	52.5	9.40	100	-	-	-

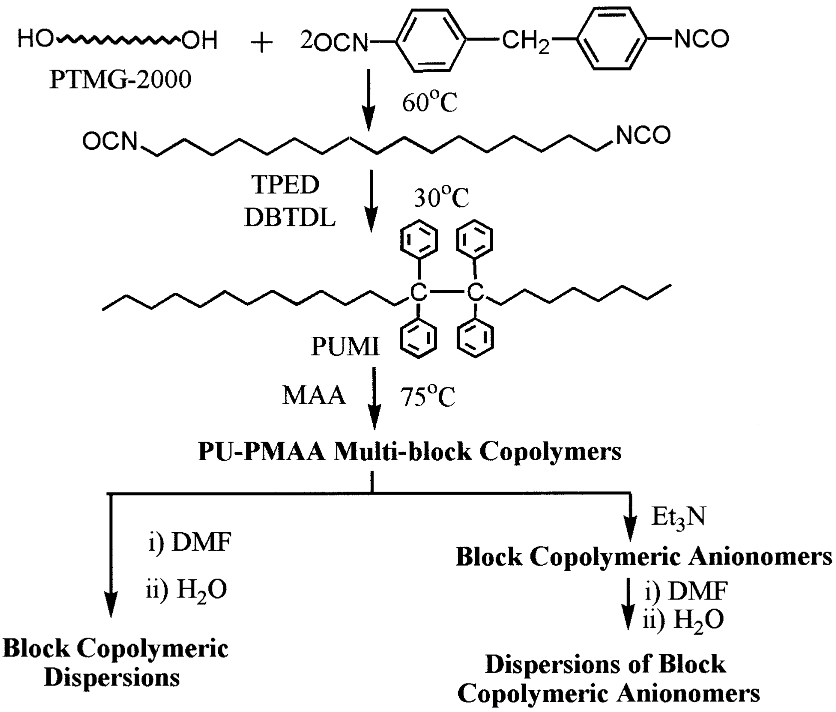
PMAA multi-block copolymers was reported elsewhere (11).

Preparation of Dispersions

6g of block copolymer or anionomer was taken in a 3 necked flask and dissolved in 24 ml of 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 of water was added. The speed of the stirrer was kept at 1000 RPM and the addition of water was carried out using a pump with constant flow rate. One part of the dispersion was taken into a teflon plate and dried at 50°C to obtain film. This film was stored at 25°C for 48 hrs in vacuum before characterizing.

Results and Discussion

Tetraphenylethane-based PU macroiniferters have been used to polymerize vinyl monomers through "living" radical mechanism (10-12). PU macroiniferter based on toluenediisocyanate and PTMG-1000 was used to polymerize MAA to obtain PU-PMAA multi-block copolymers through "living" radical mechanism (11). In this paper, preparation and properties of dispersions from PU-PMAA block copolymers and their anionomers are reported. The synthetic route used to prepare dispersions is given in Scheme 1.



Scheme 1

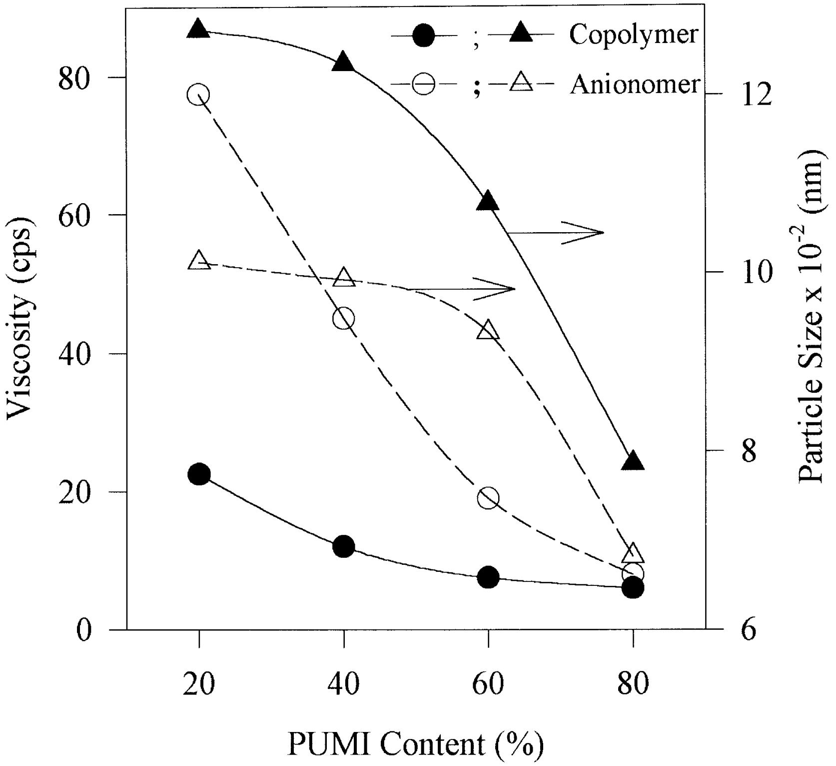


Fig. 1. Effect of PUMI content on viscosity and particle size of the dispersions of PU-PMAA multi-block copolymers and their anionomers.

Preparation, GPC results and yield of block copolymers are given in Table 1. Interestingly, PU-PMAA block copolymers and their anionomers form dispersions. As the PUMI content is increased yield also increased due to the increase of initiating species. As the PUMI content is increased, molecular weight decreased due to the increase of initiating species.

Fig. 1 shows the effect of PUMI content on particle size and viscosity of the dispersions. It is seem that viscosity as well as particle size decreases with PUMI content. In general, viscosity increases as particle size decreases due to the larger hydrodynamic volume of smaller particles. Simultaneous decrease of particle size and viscosity implys that PUMI contributes to the size reduction in one way and to the viscosity decrease in the other way. 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 despersion in water. On the other hand, PUMI block is more hydrophobic than PMAA block, and hence decreases viscosity. It seems that the latter effect viz, hydrophobicity dominate in our case. It is noted that anionomer gives smaller particle size and greater viscosity than the nonionomer, due to the hydrophilic nature of ionic groups.

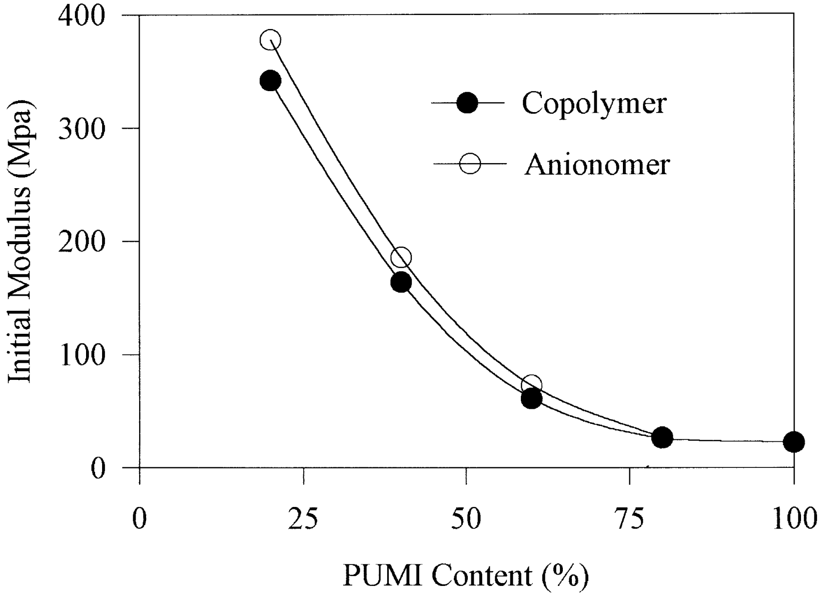


Fig.2. Initial modulus of PU-PMAA multi-block copolymers and their anionomers.

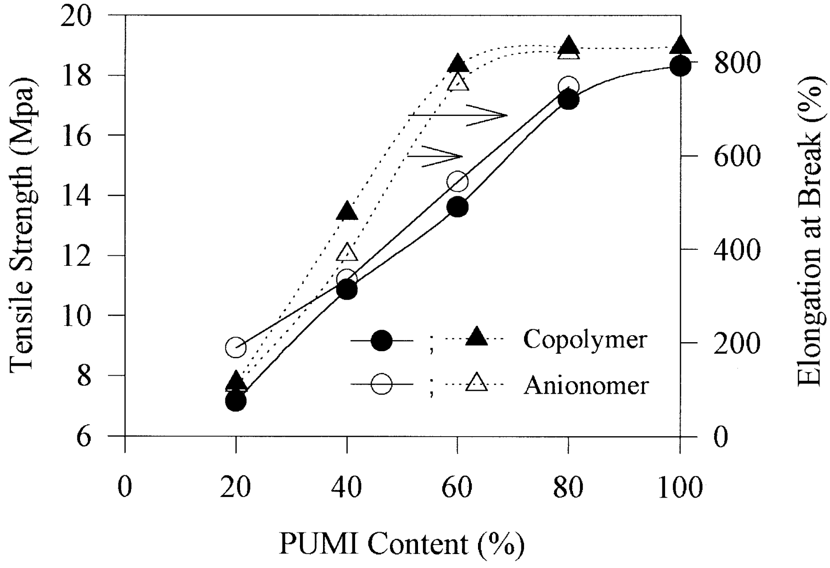


Fig. 3. Effect of PUMI content on mechanical properties of the films from the dispersions of PU-PMAA multi-block copolymers and their anionomers.

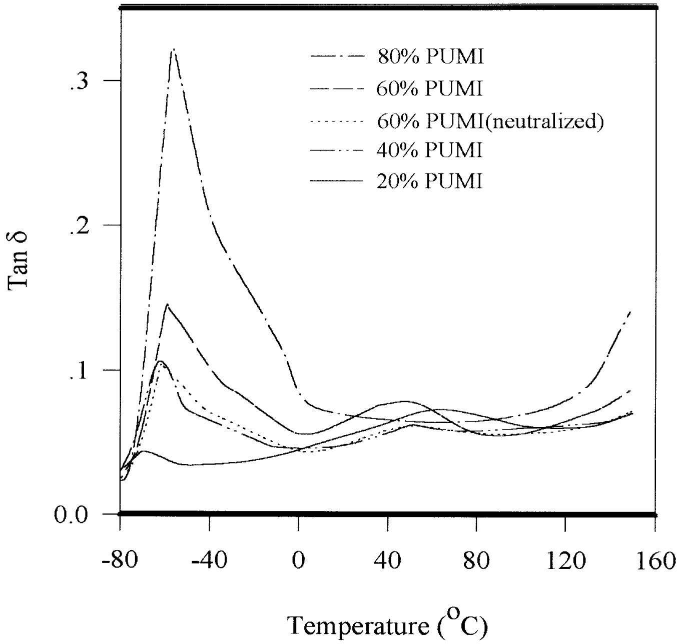


Fig. 4. Temperature-tan δ curves for PU-PMAA multi-block copolymers.

Fig. 2 shows the effect of PUMI content on the initial modulus of the films. As the PUMI content is increased, incorporation of PMA into block copolymers decreased and initial modulus of the films decreased. Anionomeric films have higher initial modulus than their corresponding block copolymers due to the Coulombic forces and greater phase seperation(to be discussed). Fig. 3 shows tensile strength and elongation at break of the films obtained from the dispersions. These properties increased as the PUMI content is increased. Since PMAA is brittle, as the percentage of PMAA block increased, the brittleness of the films also increased thereby tensile strength and elongation at break decreased. Tensile strength increses and elongation at break decreases when the block copolymers are converted into anionomers as reported already. Fig. 4 shows temperature-tan delta curves deduced from dynamic mechanical studies of the films obtained from PU-PMAA multi-block copolymeric dispersions. When PUMI feed weight decreases, Tg of the soft block decreases from -55.6 (from 80 % PUMI) to -72.3 (from 20 % PUMI). As the PUMI feed weight decreases, PMAA block length increases and hence degree of phase separation also increses. This increases phase purity between hard and soft blocks thereby Tg of the soft block decreases. The similar phase purity occurs when carboxylic groups are converted into anionomers and hence block copolymer, prepared from 60 % PUMI, has higher Tg (-58.4°C) than its corresponding anionomer (Tg=-60.6 °C) as given in fig. 4.

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