

Aqueous Dispersions of Polyurethane Polyacrylic Acid Multiblock Copolymers Through Living Radical Polymerization

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Received 18 December 2001; accepted 5 June 2002

ABSTRACT: Polyurethane macroiniferter (PUMI) including tetraphenylethane was synthesized and used to prepare polyurethane–polyacrylic acid multiblock copolymers. Film-forming aqueous dispersions without any added external emulsifiers were prepared from polyurethane–polyacrylic acid multiblock copolymers. The effect of varying PUMI content, polymerization time, and percent ionization on the properties of multiblock copolymeric dispersions were studied in detail. Interfacial tension of the dispersions and crit-

ical surface tension measurements of the films formed thereof have shown that the polymers exhibit a hydrophilic character in the dispersed phase and a hydrophobic character in the solid phase. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1109–1115, 2003

Key words: polyurethanes; aqueous dispersions; macroiniferter; block copolymers; living radical polymerization

INTRODUCTION

Polyurethanes (PUs) are of commercial interest due to their excellent properties such as high abrasion resistance, high chemical resistance, high strength, and low temperature flexibility. Normally PUs are water incompatible and are prepared using organic solvents. They can be dispersed, however, in water by incorporating hydrophilic segments.^{1,2} Due to the upcoming regulations in volatile organic emission coupled with high solvent price, these types of aqueous PU dispersions are slowly replacing conventional solvent-based systems. Aqueous PU dispersions are of three types—viz., nonionic, cationic, and anionic—depending upon the type of hydrophilic segments present in PU backbone. The synthetic methods and applications of aqueous PU dispersions are well documented.^{3–7} The main advantages of aqueous PU dispersions are that they are nontoxic, nonflammable, and eco-friendly. Moreover, these dispersions can be prepared with high molecular weights, without much change in viscosity, and with excellent scope for coating applications.

Block copolymers, which evince a lot of commercial interest,⁸ exhibit a high degree of microphase separation. In block copolymers, change in the length of the two blocks affects the degree of phase separation, phase mixing, and hard segment domain organization, which in turn leads to variation in the properties.^{9,10} In the synthesis of block copolymers through

conventional radical polymerization techniques, there is no effective control over the length of blocks. This drawback can be overcome by adopting living radical polymerization, which can be achieved by incorporating iniferter groups^{11,12} in the PU chain. Our group has reported several block copolymers using tetraphenylethane-based PU macroiniferters.^{13,14}

A block copolymer, having one of the blocks soluble in water and the other insoluble, forms micelles.^{15,16} This type of block copolymer can be prepared by incorporating vinyl blocks having ionic groups into a PU backbone. Such a block copolymer can be used to prepare aqueous dispersions and the properties of the dispersions depend on the ratio of the hydrophobic PU to hydrophilic vinyl segments. Since the block length of the ionic segment plays a major role in deciding the properties of the dispersions, the control over the block length is important. The controlled incorporation of the ionic block into PU backbone has been successfully achieved in our lab and many ionic PU block copolymers have been prepared.^{17,18}

In this article we report the synthesis and characterization of aqueous dispersions of polyurethane–polyacrylic acid (PU-PAA) multiblock copolymer where polyacrylic acid is the ionic segment. By using PU macroiniferter (PUMI), which follows living radical polymerization, the length of the ionic blocks has been altered by just varying the polymerization time.

EXPERIMENTAL

Materials

Poly(tetramethylene oxide) glycol (Aldrich, Milwaukee, USA) of molecular weight 2000 (PTMG 2000) was

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TABLE I
Synthesis and GPC Results of PU-PAA Multiblock Copolymeric Anionomers

Sample no	Polymer code	PUMI (g)	AA (g)	Time (h)	TEA (g)	% Ionization (%)	GPC Results		Conversion ^a (%)
							$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n	
1	BV 8/2	8	2	48	1.12	40	7.26	1.36	74.57
2	BV 6/4	6	4	48	2.24	40	7.81	1.27	68.82
3	BV 4/6	4	6	48	3.37	40	8.24	1.24	53.32
4	BV 2/8	2	8	48	4.49	40	8.56	1.2	41.79
5	TV 24 h	6	4	24	2.24	40	7.34	1.25	46.32
6	TV 36 h	6	4	36	2.24	40	7.64	1.27	55.54
7	TV 48 h	6	4	48	2.24	40	7.81	1.27	68.82
8	TV 72 h	6	4	72	2.24	40	7.94	1.28	79.93
9	IV 0%	6	4	48	0	0	—	—	—
10	IV 20 %	6	4	48	1.12	20	—	—	—
11	IV 40 %	6	4	48	2.24	40	—	—	—
12	IV 60 %	6	4	48	3.37	60	—	—	—
13	IV 80 %	6	4	48	4.49	80	—	—	—
14	IV 100 %	6	4	48	5.61	100	—	—	—

^a Conversion = Weight of Block Copolymer – Weight of PUMI/Weight of AA × 100.

dried under reduced pressure at 100°C before use. Toluene diisocyanate (TDI; mixture of 80% 2,4- and 20% 2,6-isomers) and dibutyltindilaurate (DBTDL; Aldrich, Milwaukee, WI, USA) were used as received. Acrylic acid (AA; SISCO, Mumbai, India) was distilled under reduced pressure and the middle portion was stored at 4°C until use. Methyl ethyl ketone (MEK) and *N,N*-dimethylformamide (DMF; Merck, Mumbai, India) were distilled and DMF was stored over molecular sieves (4 Å) until use. 1,1,2,2-Tetraphenylethane-1,2-diol (TPED) was prepared from 2-propanol and benzophenone, and the detailed procedure has been reported elsewhere.¹⁹

Characterization technique

Gel permeation chromatography (GPC; Waters, USA) attached with 410 differential refractometer and four ultrastyrigel columns (10⁶, 10⁵, 10⁴, and 10³ Å) connected in a series was used to determine the average molecular weight and molecular weight distribution. Chromatographic grade DMF (0.01% LiBr added) was used as an eluent at a flow rate of 1.0 mL/min and molecular weight calibration was done using polystyrene standards. Viscosity of the dispersions was measured using Advanced Rheometer (AR 500, TA Instruments, USA). Particle size was measured using Master sizer 2000, (Malvern Instruments, UK). Interfacial tension of the dispersions was determined by Wilhelmy plate technique. Critical surface tension (γ) of the polymer surfaces was measured from static contact angle. Contact angle was measured by a custom-built instrument and was directly read off a projected image of the liquid (volume 20 μ L), placed on the film. Strips (20 × 10 × 0.20 mm³) of each film were characterized with Dynamic Mechanical Analyzer (DMA 2980, TA Instruments, USA) using the tension film

mode in the temperature range of –100 to +100°C at a heating rate of 5°C/min, strain amplitude of 20 μ m, and frequency of 1 Hz. The Microtensile specimen (three each) for stress–strain analysis was cut at a size of 40 × 10 mm² and kept for conditioning at a temperature of 20 ± 2°C and relative humidity of 65 ± 2% for 24 h before testing. The specimen conformed to ASTM D 6385. The tensile testing was done using an Instron Universal Testing machine model 4501 at a crosshead speed of 100 mm/min.

Synthesis of PUMI

PTMG 2000 (0.04 mol, 80 g) and TDI (0.08 mol, 13.93 g) were reacted at 75°C in nitrogen atmosphere for 3 h. To this, TPED (0.04 mol, 14.65 g) was added after cooling the reaction mixture to room temperature. At the same temperature, 2 mol % (based on NCO content) of DBTDL and 183 mL of MEK (based on 40% solid content) were added and the mixture was stirred for another 24 h. The resulting PUMI was precipitated by pouring the reaction mixture into a tenfold excess of methanol. PUMI was filtered, dried under reduced pressure, and stored at 4°C until use. The detailed procedure to prepare PUMI is reported elsewhere.²⁰

Synthesis of PU-PAA multiblock copolymers and their anionomers

Calculated amounts of PUMI, DMF, and acrylic acid (Table I) were taken in a polymerization tube and degassed by passing nitrogen for 15 min. The reaction mixture was kept in a thermostated water bath at 75°C for a stipulated period. Then the reaction was arrested by quenching in ice salt mixture and calculated amount of triethylamine (Table I) was added. The solvent and the unreacted monomer were removed

TABLE II
Interfacial Tension and Critical Surface Tension Values
For PU-PAA Multiblock Copolymeric Dispersions^a

Sample no	Polymer code	Interfacial tension (mN/m)	Critical surface tension (mN/m) ^b
1	BV 8/2	42.4	26.23
2	BV 6/4	45.5	27.29
3	BV 4/6	46.5	27.80
4	BV 2/8	48.5	28.45
5	TV 24 h	44.0	25.05
6	TV 36 h	44.7	26.95
7	TV 48 h	45.5	27.29
8	TV 72 h	47.5	28.36
9	IV 0%	—	—
10	IV 20%	42.5	26.04
11	IV 40%	45.5	27.29
12	IV 60%	48.4	28.44
13	IV 80%	55.5	29.29
14	IV 100%	59.7	31.50

^a (PU-PAA) = 7 g; DMF = 21 mL, H₂O = 59.5 mL.

^b Results for the films obtained from the dispersions.

from the reaction mixture by applying vacuum. Homopolymer, if any, present in the ionic block copolymer was removed by washing thoroughly with ice cold water. The product was then dried and stored at 4°C until use.

Preparation of aqueous dispersions

A calculated amount of PU-PAA multiblock copolymeric ionomer was dissolved in DMF and the reaction mixture was homogenized by stirring for 30 min. To this, a calculated amount of water (Table II) was added dropwise at a constant rate while the stirring speed was maintained at 1000 rpm. A portion of the resulting dispersion was cast in a teflon plate and dried at 120°C in an air-circulating oven.

RESULTS AND DISCUSSION

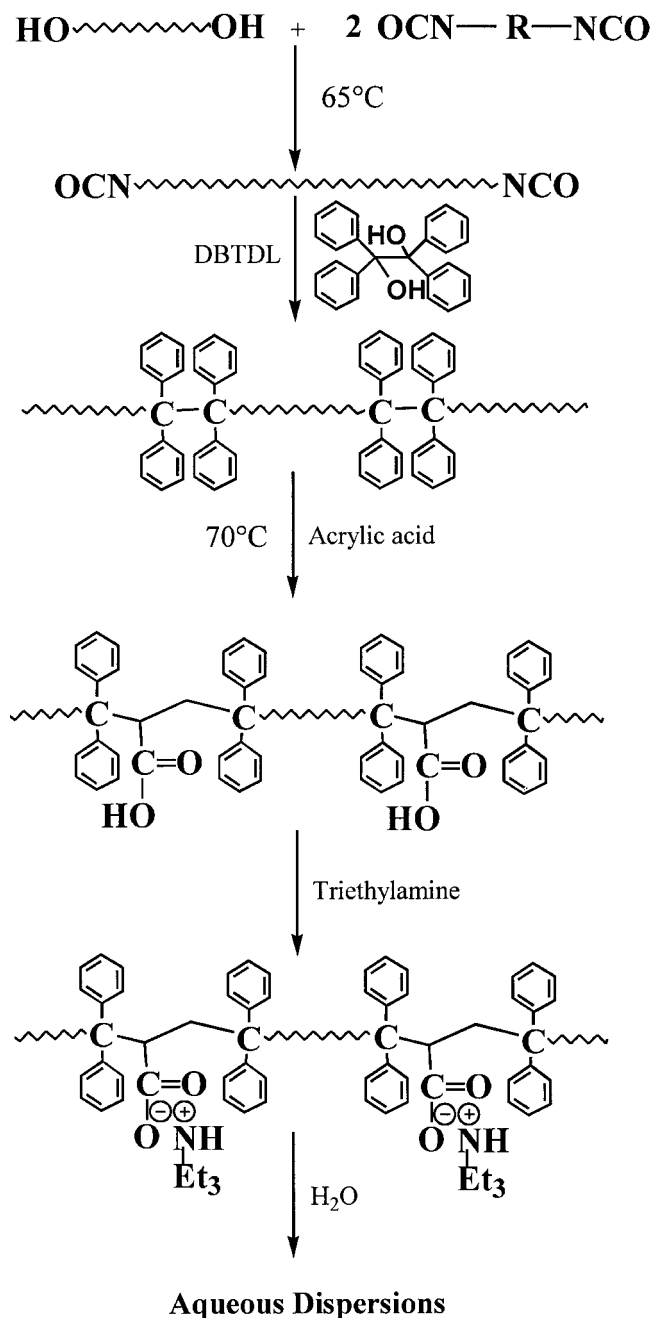
Several PU-polyvinyl block copolymers^{13,14} and PU-polyvinyl block copolymeric ionomers^{17,18} were synthesized using PUMI, and the reactions were shown to follow controlled radical mechanism. In this series, synthesis and properties of aqueous dispersions of PU-PAA multiblock copolymeric anionomers are presented. Since the amount of hydrophilic segment is the crucial factor in deciding the properties of the dispersion, living radical polymerization technique has been adopted to incorporate hydrophilic vinyl blocks into PU backbone. The synthetic route to prepare aqueous dispersion of PU-PAA multiblock copolymeric anionomers is given in Scheme 1.

Table I gives the synthetic formulations and GPC results of various block copolymeric anionomers. It is seen from the table that for a specific composition of

PUMI and acrylic acid, as the polymerization time increases there is increase in conversion and molecular weight. This is because the polymerization of acrylic acid follows controlled radical mechanism. With the decrease in PUMI content the molecular weight of the multiblock copolymers increases because as the PUMI content decreases, initiating species also decreases, thereby resulting in higher molecular weight of PU-PAA block copolymers.

Particle size and viscosity

Aqueous polyurethane dispersions are mainly used in coatings. Particle size and viscosity are important pa-



Scheme 1

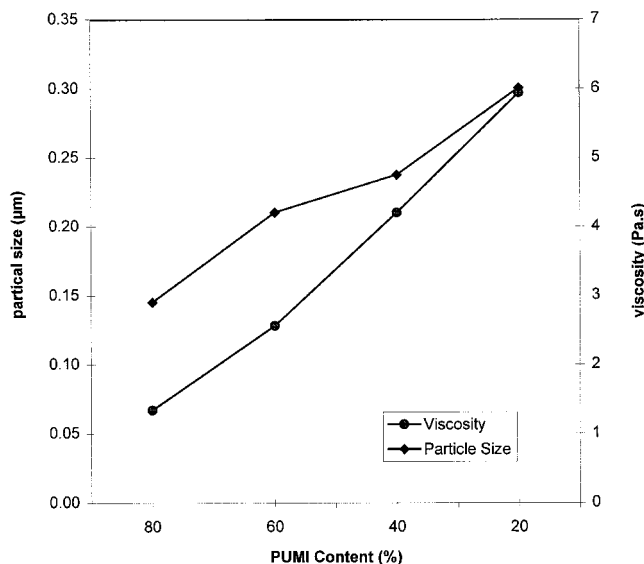


Figure 1 Effect of PUMI content on particle size and viscosity.

rameters in deciding the type of coating required. For surface coatings, larger particle size is preferred to ensure faster drying. If penetration into the substrate is required, smaller particle size is preferred. A suitable viscosity range is required to avoid sagging (in case of low viscosity) and practical difficulty in application (encountered with high viscosity).

Preparation of PU-PAA multiblock copolymeric dispersions is presented in Table II. It is interesting to note that when PU-PAA multiblock copolymers are dispersed without ionization, the dispersion is not stable. Hence all the dispersions were prepared from block copolymeric anionomers.

In general, ionic content is inversely proportional and molecular weight is directly proportional to particle size.²¹ In our case there is an increase in molecular weight as well as ionic content when PUMI content is decreased. Hence it is interesting to see the dual effect of PUMI content on the particle size of the dispersions. If ionic content plays a major role, particle size is expected to decrease with decreasing PUMI content, whereas particle size is expected to increase with decreasing PUMI content when molecular weight plays a major role. The effect of PUMI content variation on particle size and viscosity is given in Figure 1. The results show that the particle size is inversely proportional to PUMI content, which implies that the molecular weight plays a major role in this system. A similar trend was observed in the case of PU-polymethacrylic acid block copolymeric dispersions.²²

For constant molecular weight, ionic content should play a major role in deciding particle size. The effect of ionic content on particle size and viscosity is illustrated in Figure 2. It is evident from Figure 2 that at constant molecular weight, particle size decreases

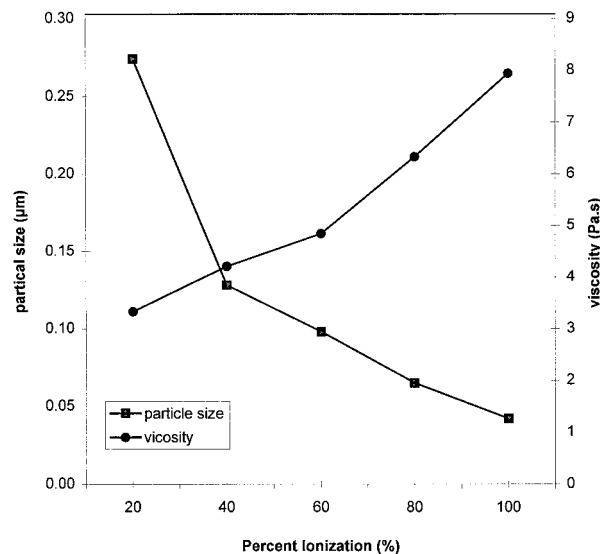


Figure 2 Effect of percent ionization on particle size and viscosity.

with increasing ionic content from 20 to 100%. Figure 3 gives the effect of polymerization time on particle size and viscosity. When polymerization time increases, molecular weight increases and hydrophilicity of the polymer also increases. Here, as in PUMI content variation particle size increases due to increase in molecular weight irrespective of the increase in hydrophilicity of the polymer.

When PUMI content decreases, molecular weight increases and hydrophilicity of the polymer also increases. It is well known that viscosity increases with increase in hydrophilicity. Though in aqueous dispersion the viscosity is not very much influenced by the molecular weight, here it is expected to have an indirect effect by affecting particle size. The relation be-

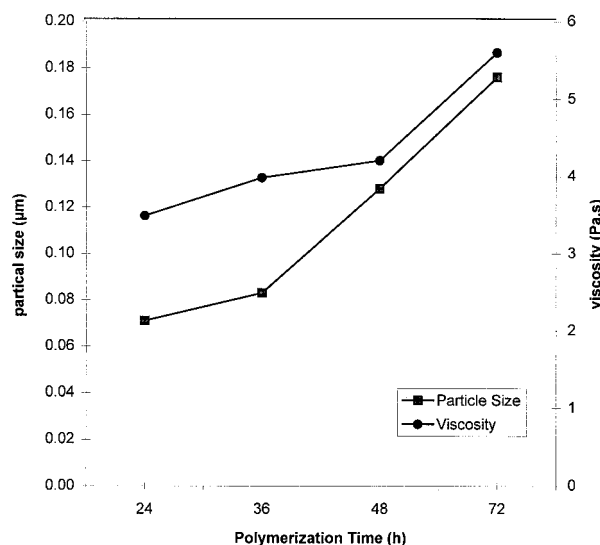


Figure 3 Effect of polymerization time on particle size and viscosity.

TABLE III
Mechanical Properties of PU-PAA Multiblock Copolymeric Anionomers

Sample no.	Polymer code	Static		Dynamic		
		Tensile strength (N/mm ²)	Elongation (%)	T_{g1}	T_{g2}	Initial storage modulus (MPa)
1	BV 8/2	5.4	1412	-57.9	46.5	796
2	BV 6/4	5.7	1098	-61.8	51.5	1424
3	BV 4/6	6.0	1048	-60.2	56.3	2243
4	BV 2/8	12.5	583	-61.5	62.8	3780
5	TV 24 h	3.2	1487	-56.3	30.4	1379
6	TV 36 h	4.8	1374	-60.4	43.7	1424
7	TV 48 h	5.7	1098	-61.8	51.6	1499
8	TV 72 h	7.4	968	-60.5	60.9	1581
9	IV 20%	3.1	983	-59.3	49.0	2935
10	IV 40%	5.7	1098	-61.8	51.5	1424
11	IV 60%	5.8	1304	-62.9	58.5	1129
12	IV 80%	7.3	1621	-64.4	63.2	707
13	IV 100%	9.6	1641	-66.3	64.7	436

tween particle size and viscosity is well established.²³ In general, when particle size increases, viscosity of the dispersion decreases. Figure 1 shows that when PUMI content decreases, viscosity of the dispersion increases irrespective of the increase in particle size. The same happens when polymerization time increases, which can be seen from Figure 3. Here, in both the cases, hydrophilicity of the polymer prevails over the indirect effect of molecular weight in controlling the viscosity. So if the molecular weight is constant, the viscosity is expected to increase with decrease in particle size. As expected, at constant molecular weight when the percent ionization is increased from 20 to 100% viscosity increases whereas the particle size decreases. The effect of ionic content on viscosity is given in Figure 2.

Interfacial and critical surface tension

Coating is an area where aqueous dispersions are mainly used. The ideal dispersion is one in which the polymer is hydrophilic when it is dispersed to enhance the pot life and the films derived from the dispersions are hydrophobic to have water-resistant qualities. These properties can be assessed by interfacial and critical surface tension (CST) measurements.

In order to understand the forces between the hydrophobic and hydrophilic segments of the polymers and their distributions at the water/polymer interface, and solid/liquid interface, studies on interfacial tension (γ) using the Wilhelmy plate technique and the critical surface tension using static contact angle measurements have been carried out. The results are given in Table II. The values clearly indicate that the polymeric dispersions show a hydrophilic character with more polar groups at the interface and thus give rise to high γ values. However, the films obtained from the dispersions indicated that the domains on the surface

are hydrophobic due to reorganization and ordering of the polymers at the solid / liquid interface. This is borne out by the low CST value of ~ 26 mN/m.

When the polymer is dispersed in water, the interfacial energy shows a high value compared to the surface energy of the cast film. The CST value increases with a decrease in PUMI content and an increase in polymerization time. There is also a notable increase in CST value when there is an increase in percent ionization. When the ionic percentage is increased from 20–100%, the interfacial tension increases, indicating the increase in hydrophilic nature of the polymer. As the polymerization time increases, interfacial tension also increases. This is because the increase in polymerization time increases the incorporation of the hydrophilic acrylic acid segments. When PUMI content decreases, the interfacial tension increases because of the fact that the incorporation of acrylic acid group increases when PUMI content is decreased.

Mechanical properties

Static mechanical analysis

Static and dynamic mechanical data of the films obtained from PU-PAA block copolymeric dispersions are presented in Table III. Generally tensile strength increases and elongation decreases with an increase in hard segment content of the polymer. When PUMI content decreases, more acrylic acid segments are incorporated in the PU backbone, thereby increasing the hard segment content of the polymer chain and hence the tensile strength increases and the elongation decreases. When percent ionization increases, ionic interactions between the polymer chains increase, leading to an increase in tensile strength and elongation. When polymerization time is increased, since the sys-

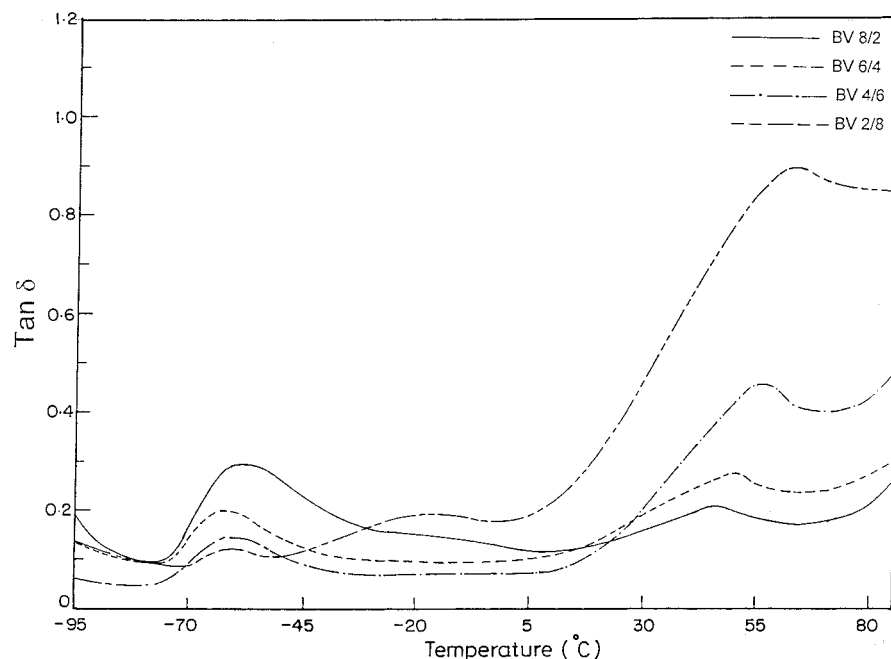


Figure 4 The $\tan \delta$ vs temperature curves of PU-PAA block copolymers with different PUMI content.

tem follows living radical polymerization, more acrylic acid units are incorporated, which results in an increase of the tensile strength and a decrease of elongation as in the case of PUMI variation.

Dynamic mechanical analysis

Figure 4 shows the effect of PUMI content variation on the dynamic mechanical characteristics of the block copolymer, and the transition temperatures are presented in Table III. All the block copolymers exhibit two transitions in the $\tan \delta$ vs temperature plot corresponding to T_g of the PU and that of the polyacrylic acid segment. Although the T_g at the high temperature region (corresponding to polyacrylic acid) increases with a decrease in PUMI content, there is not much variation in the low temperature region (corresponding to PU). One can also observe that the intensity of the $\tan \delta$ peak corresponding to the PU segment decreases while that of the polyacrylic acid segment increases with increasing acrylic acid content. This is also reflected in the initial storage modulus value (Table III), where the initial storage modulus increases with increase in acrylic acid content, suggesting the increasing rigidity of the system. Also when polymerization time increases, initial storage modulus increases, revealing that more acrylic acid units are incorporated with time.

With an increase in polymerization time, the T_g corresponding to the polyacrylic acid segment increases without much variation in the T_g of the PU segment. With increase in ionic content the T_g corresponding to PU decreases whereas T_g corresponding

to the acrylic acid segment increases due to increased microphase separation.

CONCLUSION

PU-PAA multiblock copolymeric dispersions with different block lengths and percent ionizations were prepared. GPC results confirm that the polymerization follows controlled radical mechanism. Studies show that particle size and viscosity increase with an increase in polymerization time and decreasing PUMI content. Particle size decreases and viscosity increases with an increase in percent ionization. When more acrylic acid groups are incorporated, the tensile strength increases due to more rigidity imparted by polyacrylic acid segments. The dynamic mechanical curves show two transitions corresponding to PU and acrylic acid segments. Critical surface tension and interfacial tension studies reveal that the polymers are highly hydrophilic, thus enhancing the stability of the dispersion and as films show a low critical surface energy profile, indicating the surface to be water repellent.

One of the authors (SS) thanks the Council of Scientific and Industrial Research (CSIR), India, for the award of a research fellowship.

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