Colloid Polym Sci (2002) 280: 915–921
DOI 10.1007/s00396-002-0707-y

ORIGINAL CONTRIBUTION

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Aqueous dispersions of poly(urethane-*co*-vinylpyridine) synthesised from polyurethane macroiniferter

Received: 18 December 2001
Accepted: 28 March 2002

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Abstract Polyurethane with built in iniferter fragments was synthesised and used to prepare poly(urethane-*co*-vinylpyridine). The controlled incorporation of the vinylpyridine groups was achieved by using iniferter groups. Cationomers of the block copolymers were prepared by quaternising the polyvinylpyridine groups and the ionomers were subsequently dispersed in water. The effect of varying polyurethane macroiniferter feed, polymerisation time and percent ionisation on the emulsion characteristics and the properties of the cast films were studied.

Keywords Polyurethane · Aqueous dispersion · Macroiniferter · Block copolymer · Controlled radical polymerisation

Introduction

Polyurethanes (PUs) are high-class engineering materials having a wide range of end uses. Generally they are water incompatible and are prepared using organic solvents. A number of studies have been published on the environmental effects of organic solvents. The major detrimental effects of organic solvents can be summarised into four categories namely volatile organic compounds, occupational exposure, odour and flammability. Reduction of volatile organic emission is being triggered by the increasing awareness of environmental constraints. Occupational exposure to organic solvents leads to neurological problems often referred to as Danish painter syndrome. Moreover all the solvents used to prepare coatings have a flash point around 40 °C. On account of these problems, water-borne polyurethanes are considered an alternative, which provide non-flammable eco-friendly systems with minimum occupational exposure and odour. Further, it is possible to prepare aqueous dispersions of polymers with fairly large molecular weight that have the ability to form films with superior properties and relatively low viscosity. Hence such aqueous dispersions have excellent scope in coating applications.

Normally PUs are water insoluble and one of the major raw materials, isocyanate, is highly moisture sensitive. Hence water cannot be used directly as a solvent or a diluent in reactions or applications. However, PU can be dispersed in water by using an external emulsifier or by incorporating emulsifying groups into the PU backbone [1, 2]. The latter is preferred because it does not require strong shear forces, leads to smaller particle size, has good dispersion stability and reduced water sensitivity in the films formed. Depending on the type of emulsifying groups incorporated, PU dispersions are classified as non-ionic and ionic. Ionic dispersions are further classified as anionic [3, 4], cationic [5, 6] and zwitterionic [7]. Generally the emulsifying groups are incorporated at the chain extension stage and this restricts the choice to dihydroxy/diamino compounds bearing potential ionic centres. To extend the range of possible monomer combinations, vinyl monomers containing ionic groups can be considered. The PU backbone should incorporate initiating groups such as macroazo initiators [8, 9]. Since the amount of ionic groups plays a major role in deciding the properties of the dispersions, control over the incorporation of vinyl monomers is essential. Macroazo initiators do not allow effective control over the incorporation of vinyl monomers. To effect controlled incorporation of vinyl monomers, high chemoselectivity, regioselectivity and stereoselectivity are required [11, 12]. These can be achieved by reversible deactivation of growing free radicals [11]. Iniferters can be used as reversible deactivators and hence control over incorporation of the monomers can be achieved [13, 14]. Tetraphenylethane is one such iniferter group and our group has reported synthesis of several block copolymers [15,16] and polyurethane ionomers [17, 18] with specific spatial architecture of ionic groups using tetraphenylethane-based polyurethane macroiniferters (PUMI). Aqueous dispersions of poly(urethane-*co*-methacrylic acid) anionomers synthesized through PUMI have been reported [19]. In this article the synthesis and properties of aqueous dispersions of poly(urethane-*co*-vinylpyridine) (PU-PVPy) cationomers have been reported.

Aqueous polyurethanes are gaining popularity and various reviews have come out in this field on the synthesis and commercial applications of these products [6, 20, 21]. Anionomeric dispersions are often encountered in the literature and there are only few reports on cationic PU dispersions. Cationic PU dispersions show very high adhesion to various ionic substrates, especially anionic substrates such as leather and glass. They also find applications in many areas such as blends, additives etc. Since the amount of hydrophilic segment plays a major role in deciding the properties of the dispersion, control over the incorporation of ionic moieties into the PU backbone was achieved through the iniferter-based controlled radical polymerisation technique.

Experimental

Materials

Poly(tetramethylene oxide)glycol (Aldrich, USA) of molecular weight 2000 (PTMG 2000) was 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, USA) were used as received. Vinylpyridine (Vpy) (Aldrich, USA) 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, 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 [22].

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 25 °C. Then 2 mol % (based on NCO content) of DBTDL and 183 ml MEK (based on 40% solid content) were added and the mixture was stirred for another 24 h at 25 °C. The resulting PUMI was precipitated by pouring the reaction mixture into ten-fold excess of methanol. PUMI was filtered, dried under reduced pressure and stored at 4 °C until use.

Synthesis of poly(urethane-*co*-vinylpyridine) and their cationomers

Calculated amounts of PUMI, DMF and VPy (cf.Table 1) were taken in a polymerisation 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 it in ice salt mixture. A calculated amount of bromobutane (cf. Table 1) was added and the quaternisation reaction was carried out for 24 h. The solvent was removed from the reaction mixture under vacuum. Homopolymer, if any, present in the ionic block copolymer was removed by washing thoroughly with methanol. The product was then dried and stored at 4 °C until use.

Table 1. Composition, codes and GPC results of PU-VPy cationomers

S. No	Polymer code	PUMI	VPy	Time	Bromo butane	% Ionisation	GPC results		Conversion[a]
		(g)	(g)	(h)	(g)	(%)	$M_n \times 10^{-4}$	M_w/M_n	(%)
1	BV 8/2	8	2	48	1.56	60	5.85	1.42	78.09
2	BV 6/4	6	4	48	3.12	60	6.91	1.30	65.63
3	BV 4/6	4	6	48	4.69	60	7.76	1.29	56.57
4	BV 2/8	2	8	48	6.26	60	8.82	1.31	48.35
5	TV 24 h	6	4	24	3.12	60	5.15	1.33	41.58
6	TV 36 h	6	4	36	3.12	60	6.01	1.32	59.78
7	TV 48 h	6	4	48	3.12	60	6.91	1.30	65.63
8	TV 72 h	6	4	72	3.12	60	7.86	1.31	74.35
9	IV 0%	6	4	48	0	0	–	–	–
10	IV 20%	6	4	48	1.04	20	–	–	–
11	IV 40%	6	4	48	2.08	40	–	–	–
12	IV 60%	6	4	48	3.12	60	–	–	–
13	IV 80%	6	4	48	4.17	80	–	–	–
14	IV 100%	6	4	48	5.21	100	–	–	–

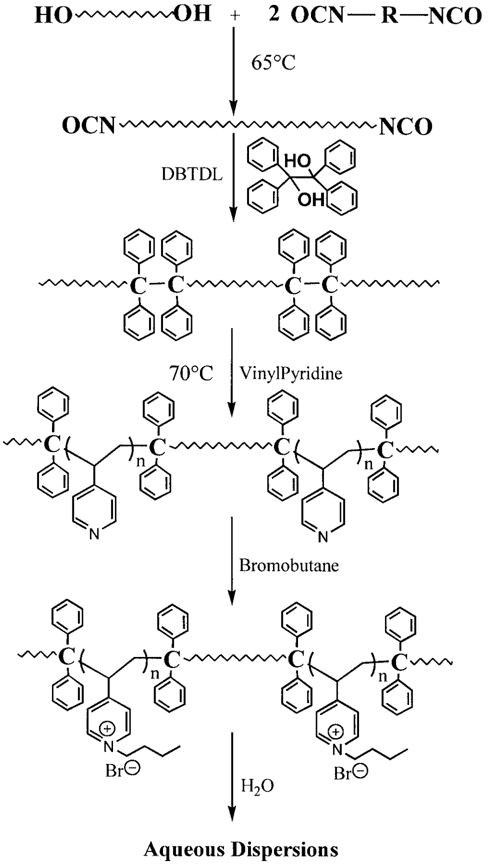
[a] Conversion = [(Weight of blockcopolymer−weight of PUMI)/(Weight of vinylpyridine)]×100

Preparation of aqueous dispersions

PU-PVPy multiblock copolymeric cationomer (6 g) was dissolved in 21 ml DMF and the reaction mixture homogenised by stirring for 30 min. To this, 59 ml water was added drop wise at constant rate while the stirring speed was maintained at 1000 rpm. Portion of the resulting dispersion was cast in a Teflon plate and dried at 120 °C in an air-circulating oven.

Characterisation techniques

Gel permeation chromatography (GPC, Waters, USA) attached with 410 differential refractometer and four ultra styragel columns (10^6 Å, 10^5 Å, 10^4 Å and 10^3 Å) connected in 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 ml), placed on the film. Strips (20×10×2 mm^3) of each film were characterised with dynamic mechanical analyzer (DMA 2980, TA Instruments, USA) using the tension film mode in the temperature range of –100 °C to + 100 °C at a heating rate of 5 °C per minute, strain amplitude of 20 μm and frequency of 1 Hz. The microtensile specimens (three each) for stress–strain analysis were cut at a size of 40 mm×10 mm 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.



Scheme 1. Synthesis of aqueous dispersions of PU-PVPy block copolymers

Results and discussion

The synthetic route for preparation of an aqueous dispersion of PU-PVPy cationomers is given in Scheme 1. The dispersion with composition 6 g PU and 4 g Vpy that was polymerised for 48 h (PU6/4, 48 h) was taken and the ionic percentage varied from 0% to 100%. The polymer with 0% ionisation did not form a dispersion, whereas, the dispersions obtained from compositions with ionic content of 20% and 40% settled within 4 days and 10 days, respectively. Hence all other dispersions were prepared from cationomers of 60% ionisation and more.

Table 1 gives the compositions and GPC results of various block copolymeric cationomers. In this system both conversion and molecular weight increased with increasing polymerisation time. This is a typical result of controlled radical polymerisation. When PUMI feed decreased, the amount of initiating species decreased and hence molecular weight increased and the conversion decreased.

Particle size and viscosity

Particle size and viscosity are inter-related properties of the aqueous PU dispersions. They are of practical importance and have influence on the properties of the dispersion and the films derived from it. Pot-life and the film-forming tendencies are higher for dispersions with smaller particle size while larger particles facilitate faster drying and hence find application in surface coatings.

Figure 1 gives the effect of PUMI feed on particle size and viscosity of the dispersions. When PUMI feed decreased, the viscosity of the dispersion decreased and the particle size increased. Molecular weight of the polymer increased with decreasing PUMI feed and hence the viscosity of the polymer solution in organic solvent increased. Solution viscosity directly contributes to the break-up of the dispersed phase. Assuming the stress continuity at the interface during phase inversion, larger dispersed phase (polymer solution) viscosity over the continuous phase (aqueous phase) leads to smaller dispersed phase deformation leading to larger particle size according to

$$\eta_c \gamma_c = \eta_d \gamma_d \tag{1}$$

where η_c and η_d are the viscosities of the continuous phase and dispersed phase and γ_c and γ_d are the shear rates experienced by the continuous phase and dispersed

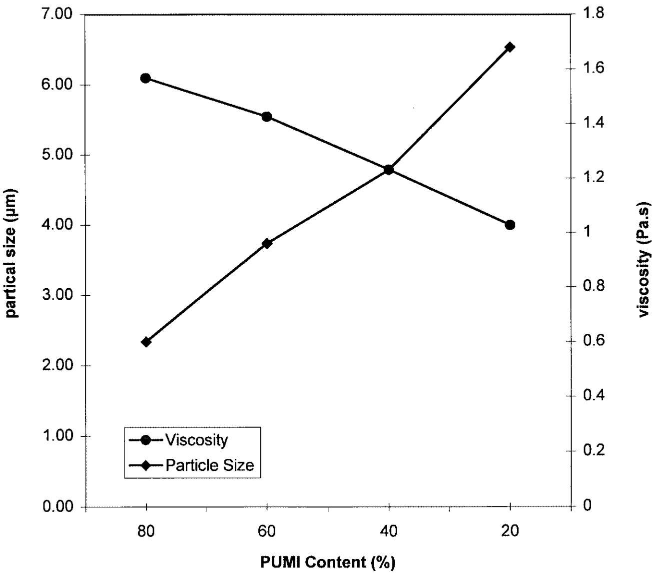


Fig. 1. Effect of PUMI content on particle size and viscosity

phase [23]. When particle size increased, viscosity of the dispersion decreased due to smaller total effective volume of the particle. So when PUMI feed decreased, particle size increased and hence viscosity decreased.

The effect of polymerisation time on the particle size and viscosity is given in Fig. 2. When polymerisation time increased, particle size increased and the viscosity of the dispersion decreased. Since the polymerisation of the VPy follows a controlled radical polymerisation mechanism, the molecular weight of the polymer increased with an increase in polymerisation time. As in the case of PUMI feed variation, an increase in molecular weight led to coarse particles and in turn the viscosity of the dispersion decreased.

When ionic content is increased from 20% to 100%, at a constant molecular weight, particle size decreased and the viscosity increased. Generally the average particle size of the dispersion decreases with increasing ionic content. The ionomer dispersions are stabilised by formation of an electrical double layer. When ionic content increases the thickness of the electrical double layer increases and swelling of the particle in water also increases. These contribute to the increase in effective hydro-dynamic volume of the dispersion and hence the viscosity of the dispersion increases. Figure 3 gives the effect of percent ionisation on the particle size and viscosity of the dispersions.

Interfacial tension and critical surface tension

The ratio of the hydrophilicity to hydrophobicity of the polymer is crucial in determining the dispersion and film properties. Increase in hydrophilicity enhances the storage stability whereas increase in hydrophobicity is desired to avoid swelling of the coated films in a moisture-prone atmosphere. For an ideal dispersion there should be a perfect balance between hydrophilicity and hydrophobicity. The hydrophilic/hydrophobic nature of the polymer in the dispersed state and as a cast film can be determined by the interfacial tension (IFT) 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

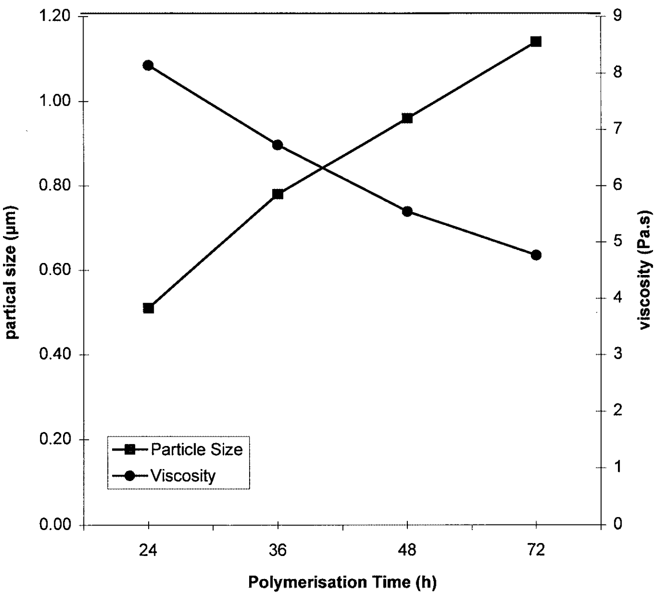


Fig. 2. Effect of polymerisation time on particle size and viscosity

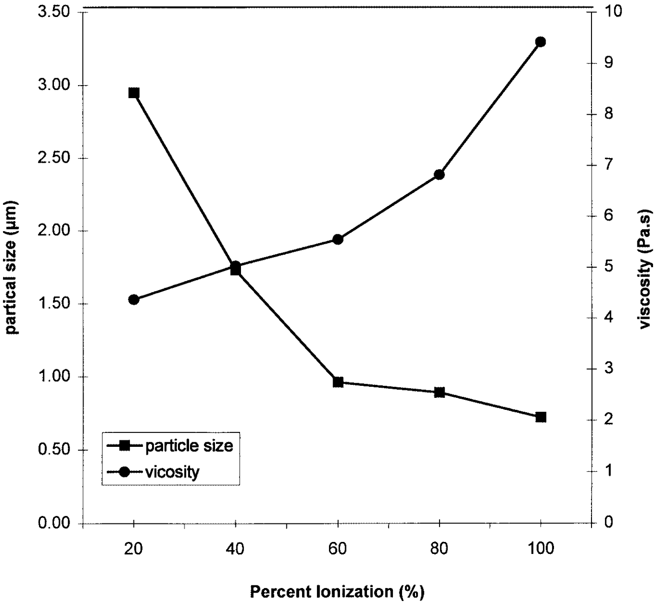


Fig. 3. Effect of percentage ionisation on particle size and viscosity

and the solid/liquid interface, studies on IFT (using the Wilhelmy plate technique) and CST (using static contact angle measurements) have been carried out. The results are given in Table 2. The values clearly indicate that the dispersions show a hydrophilic character with more polar groups at the interface thus giving rise to high g values. However, the films obtained from the dispersions indicated that the hydrophobic domains are present predominantly on the surface, possibly due to reorganisation and ordering at the solid/liquid interface. This is borne out by the low CST value of ~20 mN/m.

When percent ionisation was increased from 20% to 100%, interfacial tension and the critical surface tension values increased suggesting an increase in the hydrophilicity of the polymer. However, the change in the CST and IFT values with the change in the PUMI feed and polymerisation time were insignificant. This is because unless quaternised, VPy does not contribute to the hydrophilicity of the polymer whereas after quarternisation it becomes an ionic centre and imparts hydrophilicity to the polymer. So when the quaternisation with bromobutane is kept constant there is no notable increase in the hydrophilicity of the polymer with increasing VPy content.

Mechanical properties

Static mechanical analysis

Tensile strength and elongation at break values of the various compositions are listed in Table 2. When PUMI content decreased, more VPy groups were incorporated in the PU backbone leading to an increase in the hard segment content of the PU. Hence, the tensile strength increased and the elongation decreased. In PU, the hard segments contribute to the strength and high-temperature properties whereas the soft segments contribute to the low-temperature properties. Hence tensile strength increased with increase in hard segment content. When polymerisation time increased, more VPy groups were incorporated, accounting for the increase in tensile strength and decrease in elongation as in the case of PUMI feed variation. With an increase in percentage ionisation, both the tensile strength and elongation increased. The simultaneous increase of elongation and tensile strength implies that the ionic interactions between the polymer chains increases with increasing percentage ionisation.

Dynamic mechanical analysis

The dynamic mechanical properties of PU-PVPy cationomers are listed in Table 2. Two transitions were observed for all the compositions of the block copolymeric cationomers: the low temperature transition is related to Tg of the PU segment while the high temperature transition is due to the PVPy segment. Figure 4 gives the tan δ vs. temperature plots for the PUMI content variation. When PUMI feed decreased, transition at low temperature remained unaltered while the high temperature transition shifted from 45 °C to 58 °C. This increase in high temperature transition is due to incorporation of more VPy units thus increasing the length of VPy blocks with decrease in PUMI content. It was evident that the intensity of tan δ peak corresponding to PU segment decreased while that of the VPy segment increased with increasing VPy content. This was also reflected in storage modulus vs. temperature plots (Fig. 5) where the

Table 2. Interfacial tension value for the PU-PVPy cationomer dispersions and critical surface tension & static and dynamic mechanical properties of the dispersion cast films

S. No	Polymer code	Critical surface tension (mN/m)	Interfacial tension (mN/m)	Mechanical properties			
				Static		Dynamic	
				Tensile strength (N/mm)	Elongation (%)	Tg_1	Tg_2
1	BV 8/2	23.15	51.50	3.494	1259	–68.79	45.61
2	BV 6/4	24.25	50.50	4.923	1034	–67.36	49.83
3	BV 4/6	22.14	51.50	5.792	848	–67.52	54.65
4	BV 2/8	23.65	49.00	6.675	484	–68.98	58.92
5	TV 24 h	23.00	52.50	2.162	1364	–69.30	39.43
6	TV 36 h	23.45	53.50	4.059	1098	–70.28	47.56
7	TV 48 h	24.25	50.50	4.923	1034	–67.36	49.83
8	TV 72 h	22.85	50.50	5.465	868	–68.79	56.97
9	IV 20%	20.14	46.60	2.276	593	–62.79	44.31
10	IV 40%	21.49	47.90	2.605	762	–65.10	45.93
11	IV 60%	24.25	50.50	4.923	1034	–67.36	49.83
12	IV 80%	26.23	54.70	5.569	1276	–69.95	54.73
13	IV 100%	29.5	57.90	6.27	1416	–72.28	58.70

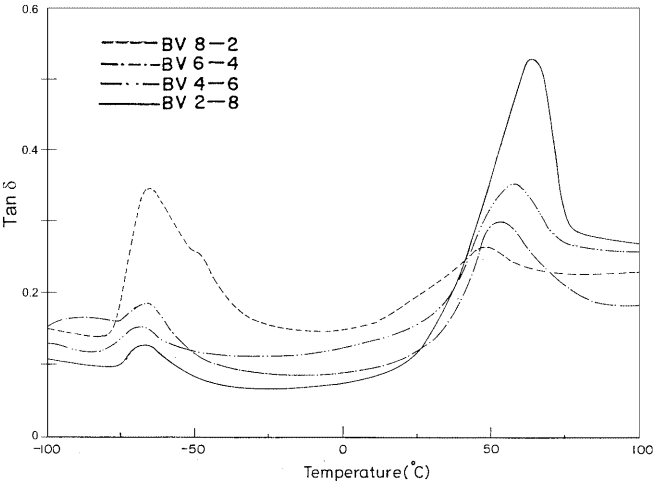


Fig. 4. Tan δ vs. temperature curves of PU-PVPy block copolymers with different PUMI content

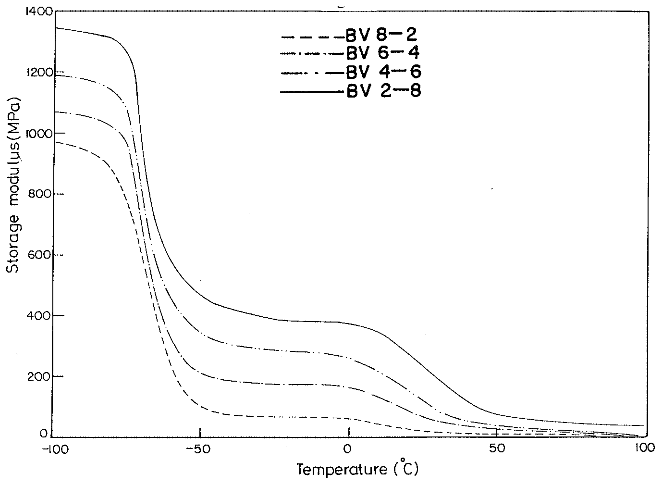


Fig. 5. Storage modulus vs temperature curves of PU-PVPy block copolymers with different PUMI content

initial storage modulus increased with increasing VPy content suggesting the increasing strength of the system with increase in VPy incorporation. A similar trend was observed in the case of time variation. With an increase in polymerisation time more VPy groups were incorporated into the PU chain leading to an increase in Tg at the high-temperature region. When percentage ionisation increased from 20% to 100% Tg of PU shifted to lower temperatures and that corresponding to the PVPy shifted to higher temperatures due to microphase separation. When ionic content increases, due to charge repulsion between the N+ groups, realignment of hydrogen bonding and columbic forces takes place leading to rod-like entities and resulting in increased microphase separation [24].

Conclusion

Poly(urethane-*co*-vinylpyridine) cationomers have been synthesised using tetraphenylethane-based PUMI and the same dispersed in water to obtain PU-PVPy dispersions. The polymerisation of VPy proceeded via controlled radical mechanism, which was evident from the increase in molecular weight and conversion with increase in polymerisation time. Particle size increased and viscosity decreased with an increase in the molecular weight of PU-PVP. Particle size decreased and viscosity increased when percent ionisation increased. Tensile strength was found to increase with the increase in PVPy blocks. The dynamic mechanical curves were indicative of a system with two-phase morphology. CST and IFT studies revealed that although the polymers were reasonably hydrophilic in dispersed state, they exhibited a low critical surface energy profile when cast as films. This indicates that the surface is predominantly hydrophobic in nature.

Acknowledgements The author (S. Sundar) thanks the Council of Scientific and Industrial Research, New Delhi, India, for the award of senior research fellowship.

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