Available online at www.sciencedirect.com

Polymer 46 (2005) 11294–11300

polymer

www.elsevier.com/locate/polymer

Preparation of stable polyurethane–polystyrene copolymer emulsions via RAFT polymerization process

Yu-Zi Jin [a,b], Yoon Bong Hahn [a], Kee Suk Nahm [a], Youn-Sik Lee [a,*]

[a] *Division of Environmental and Chemical Engineering, Nanomaterials Research Center, Chonbuk National University, Chonju 561-756, South Korea*
[b] *Department of Chemistry, College of science, Yan Bian University, Yanji 133-002, People's Republic of China*

Received 21 June 2005; received in revised form 7 October 2005; accepted 8 October 2005
Available online 27 October 2005

Abstract

Stable polyurethane–polystyrene (PU–PS) copolymer emulsions were prepared by the polymerization of 2-hydroxyethyl acrylate (HEA)-capped PU macromonomer and styrene, using azobis(isobutyronitrile) (AIBN), a radical initiator, and 4-((benzodithioyl)methyl)benzoic acid, a reversible addition–fragmentation chain transfer (RAFT) agent. As the molar ratio of the RAFT agent to AIBN increased, the zeta potential of the resulting copolymer emulsion increased, but the average size and size distribution of the emulsion droplets decreased. A living polymerization of HEA end-capped PU macromonomer and styrene was characterized by a linear increase in the molecular weight and decrease in the molecular weight distribution with consumption of monomers. The tensile strength, hardness and water-resistance of the copolymer films, prepared from the PU–PS copolymer emulsions, were much greater than those of the films prepared from the pure PU emulsion. The copolymer emulsions, prepared via the RAFT polymerization process, are expected to exhibit better storage stability than those prepared via the conventional free radical polymerization process, due to the presence of carboxyl groups derived from the RAFT agent at the PS block termini.

Keywords: Living polymerization; PU macromonomer; RAFT process

1. Introduction

Water-borne polyurethanes (PUs) continue to expand their use as applications in coatings and adhesives, mainly due to the trend of environmental regulations that require a decrease in the level of solvent emissions [1–3]. Cationic [4], anionic [5,6], and zwitterionic [7] PUs have been used successfully to prepare dispersions. However, their performances, including water-resistance, are usually inferior to solvent-borne coating films, due to the presence of hydrophilic groups in the PU chains, or surfactants added for dispersion stability. One of the strategies implemented to improve the performance of the water-borne PUs is to prepare PU-vinyl polymer hybrid emulsions, where the two different polymers are physically mixed (e.g. interpenetrating networks) or covalently linked (e.g. graft copolymers). The grafting approach can be achieved via free radical copolymerization between vinyl-terminated PU macromonomers and vinyl monomers, such as styrene (ST) and acrylates [8,9].

Recent progress in 'living' free-radical polymerization techniques, such as atom-transfer radical polymerization (ATRP) [10], nitroxide-mediated radical polymerization (NMP) [11], and reversible addition–fragmentation chain transfer (RAFT) polymerization [12,13], have created new avenues for the synthesis of vinyl polymers with predefined molecular weights, well-defined end groups, and narrow polydispersities. Emulsion polymerizations of vinyl monomers via RAFT process, have already been reported in the previous literature [14–16].

It may be of interest to prepare PU-vinyl polymer hybrid emulsions using the RAFT process, since the incorporation of a RAFT agent, containing hydrophilic groups such as carboxyl groups, into the hybrid, may enhance the stability of the resulting polymer emulsions. To our best knowledge, however, there is no report on the application of the RAFT polymerization process to the preparation of PU-vinyl polymer hybrid emulsions.

In this research, we attempted to apply the RAFT process to the preparation of PU–polystyrene (PU–PS) copolymer emulsions. The HEA end-capped PU macromonomers were reacted with ST in the presence of various molar ratios of

---

[*] Corresponding author. Tel.: +82 63 270 2312; fax: +82 63 270 2306.
E-mail address: yosklear@chonbuk.ac.kr (Y.-S. Lee).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.10.049

a carboxyl-containing RAFT agent to a free radical initiator. This paper describes the synthesis and general characteristics of the resulting PU–PS copolymer emulsions.

2. Experimental section

2.1. Materials

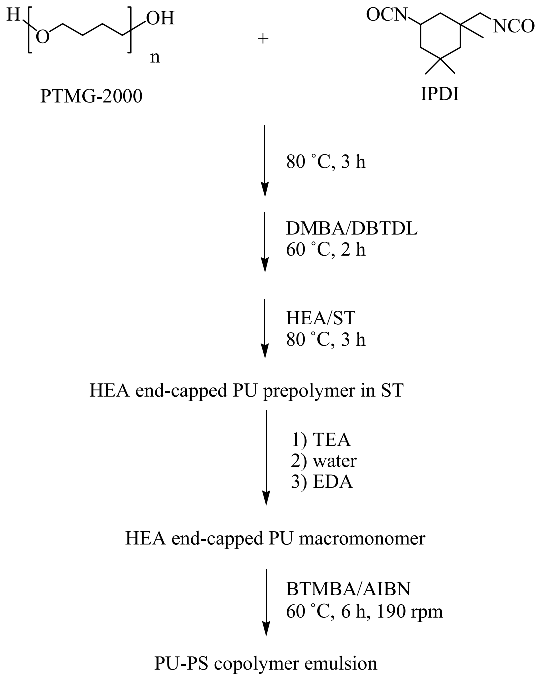
The raw materials used for this study are listed in Table 1. Dimethylolbutyric acid (DMBA) was dried in a vacuum state at 100 °C for 3 h before use. 2-Hydroxyethyl acrylate (HEA) and ST monomers were purified by passage through activity I neutral alumina (to remove inhibitors), followed by fractional distillation, and then distilled immediately prior to use. The other chemicals were all analytical grades and used as received from suppliers. 4-((Benzodithioyl)methyl)benzoic acid, a RAFT agent, was prepared in our laboratory, according to the previous publication [17].

2.2. Preparation of PU–PS copolymer emulsions via RAFT process

The polymerization reaction was conducted in a 500 ml four-necked flask equipped with a reflux condenser, a mechanical stirrer, a thermometer and a nitrogen gas inlet. The polymerization procedure and recipes are presented in Scheme 1 and Table 2, respectively. A mixture of poly(tetramethylene glycol) of M_n 2000 (PTMG-2000) and isophorone diisocyanate (IPDI) was stirred at 80 °C for 3 h, and cooled to 60 °C, followed by the addition of DMBA and a few drops of dibutyltin dilaurate (DBTDL) as catalyst. The mixture was stirred at 60 °C for 2 h, and heated to 80 °C, followed by the addition of ST and subsequently HEA. The reaction was conducted further at 80 °C for 3 h. The PU prepolymer was neutralized with triethylamine (TEA), followed by the addition of deionized water and ethylene diamine (EDA) to obtain HEA end-capped PU macromonomer dispersion (PUD). The solid content (PU macromonomer plus ST) of the dispersion was adjusted to be 25 wt% by the addition of calculated amount of deionized water. A mixture of PUD, 2,2-azobisisobutyronitrile (AIBN) and BTMBA was mechanically stirred at 190 rpm and 60 °C for 6 h, to obtain the PU–PS copolymer emulsions.

Table 1
Raw materials

Designation	Chemical description	Supplier
PTMG-2000	Poly(tetramethylene glycol)	Duksung Co. Ltd (South Korea)
HEA	2-Hydroxyethyl acrylate	Aldrich
DMBA	Dimethylolbutyric acid	Aldrich
IPDI	Isophorone diisocyanate	Junsei Chemical Co., Ltd (Japan)
TEA	Triethylamine	Aldrich
ST	Styrene	Aldrich
DBTDL	Dibutyltin dilaurate	Duksung Co. Ltd (South Korea)
EDA	Ethylene diamine	Aldrich
AIBN	2,2-Azobisisobutyronitrile	Aldrich



Scheme 1. Synthetic route to PU–PS copolymer emulsions.

2.3. General measurements

FT-IR and ^{1}H NMR spectra of the synthesized RAFT agent and polymers were recorded on a JASCO FT-IR spectrometer and a JEOL-JMN 400 MHz spectrometer, respectively. The average molecular weights (M_w and M_n) of the copolymers, obtained by drying the polymer emulsions, were measured by gel permeation chromatography (GPC, Maxima 820), calibrated with polystyrene standards, using chloroform as solvent. The thermal transitions of the polymers were observed by differential scanning calorimetery (DSC, DuPont 2000). Each polymer sample (3–8 mg) was sealed in an aluminum pan and was heated at a rate of 20 °C/min under a nitrogen purge of 60 ml/min.

2.4. Emulsion droplet size and zeta potential measurements

The droplet size and the zeta potential of the polymer emulsions were measured using dynamic light scattering technique (DLS-8000, Otuska). For measurement of emulsion droplet size, the emulsions were diluted with deionized water to adjust the solid content to be around 1 wt%, and then placed in a cell. The temperature of the cell was kept at around 25 °C and the measuring time was 300 s. The zeta potentials were measured at an angle of 90° at room temperature after the original emulsions were diluted to around 10,000 times with deionized water.

Table 2
Recipes for synthesis and results obtained from GPC and DSC experiments

Sample codes	PTMG-2000/ IPDI/DMBA/ HEA/TEA/EDA (mol)	ST (mol)	AIBN (wt%)	[BTMBA]/ [AIBN] (mol/mol)	Size of emulsion droplet (nm)	M_n	PDI (M_w/M_n)	T_{g1}, T_{g2} (°C)	T_m (°C)
PU macro-monomer	7/18/6/4/6/3	0	0	–	62	4000	2.4	−76, –	–
PU-PS-0	7/18/6/4/6/3	40	5	0	95	27,000	4.7	−77, 102	24
PU-PS-1	7/18/6/4/6/3	40	5	1	92	25,000	3.0	−76, 101	25
PU-PS-3	7/18/6/4/6/3	40	5	3	91	20,000	2.8	−74, 98	25
PU-PS-5	7/18/6/4/6/3	40	5	5	87	19,000	2.3	−74, 100	26
PUD	10/18/5/0/5/3	–	–	–	58	24,000	1.9	−76, –	23

2.5. Tensile property measurements

The polymer emulsions were cast on silicon plates, and dried at room temperature for 1 week. The resulting polymer films were further dried in a vacuum oven at 60 °C for overnight. The tensile strength and elongation at the break were measured with a universal test machine (Lloyd Co.) at room temperature with a crosshead speed of 50 mm/min. For each data point, five samples were tested, and an average value was taken.

2.6. Water absorption measurements

The dried polymer films (20 mm×20 mm), prepared as described above, were immersed in water at 23 °C for 24 h. After the residual water was wiped from the films using filter paper, the weight (W_1) of the wet film was measured immediately. The water absorption, R (%), was calculated as follows:

$$R(\%) = \left[\frac{W_1 - W_0}{W_0}\right] \times 100$$

where W_0 represents the weight of the dried film before immersion in water.

3. Results and discussion

As outlined in Scheme 1, an excess amount of IPDI was reacted first with PTMG-2000, and then DMBA and finally HEA, to form HEA end-capped PU prepolymer. Subsequently, TEA, a calculated amount of water and finally EDA were added to the above mixture, for neutralization of the COOH groups in DMBA units, dispersion in water, and chain extension, respectively, to obtain HEA end-capped PU macromonomer dispersion with solid content of 25 wt%. The disappearance of the NCO absorption peak at 2250–2270 cm^{-1} was confirmed using FT-IR spectroscopy, indicating that the chain-extension reaction was completed to form HEA end-capped PU macromonomer dispersion (PUD). A mixture of PUD, AIBN and BTMBA was mechanically stirred at 190 rpm and 60 °C for 6 h, to obtain the PU–PS copolymer emulsions.

The ^{1}H NMR and FT-IR spectra of HEA end-capped PU macromonomer and PU-PS-5 are shown in Figs. 1 and 2, respectively. The NMR spectrum of HEA end-capped PU macromonomer exhibits three vinyl proton peaks in the range of 5.8–6.5 ppm. The chemical shifts and splitting patterns indicate clearly the existence of the HEA end groups at both ends of the PU macromonomer. On the other hand, the NMR spectrum of PU-PS-5 does not exhibit any vinyl proton peaks in the same range as above. Instead, it exhibits aromatic proton peaks in the range of 7.0–8.3 ppm, corresponding to the incorporated ST units and the RAFT moieties. This result

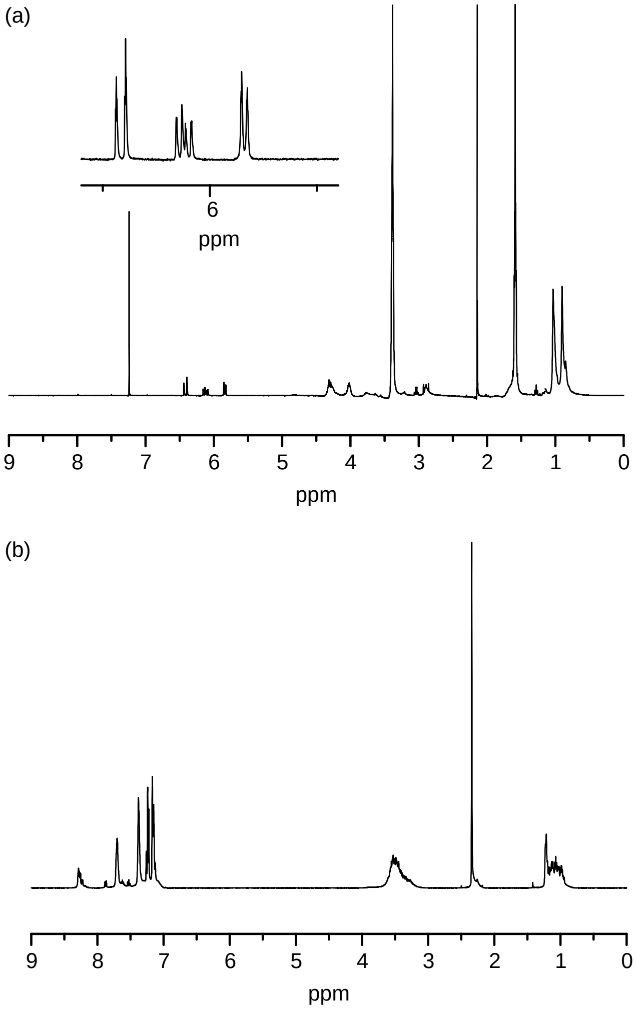


Fig. 1. ^{1}H NMR spectra of (a) PU macromonomer and (b) PU-PS-5.

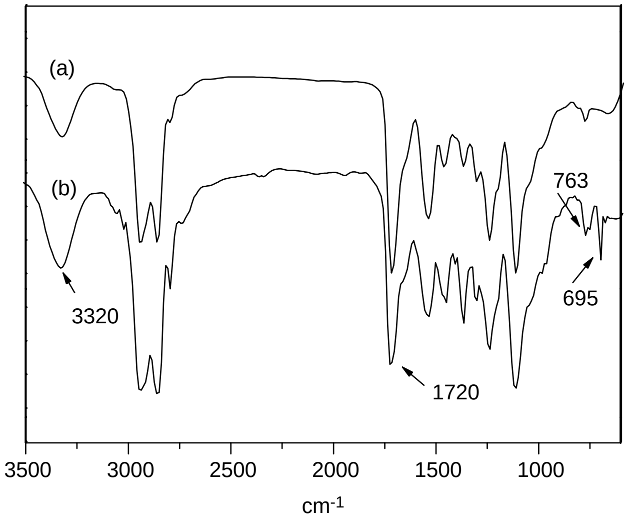


Fig. 2. FT-IR spectra of (a) PU macromonomer and (b) PU-PS-5.

indicates that HEA end-capped macromonomers were completely reacted with ST monomers. Two FT-IR spectra in Fig. 2 show the characteristic absorption peaks of urethane bonds at 3320 and 1720 cm^{-1}. However, PU-PS-5 exhibits two peaks at 763 and 695 cm^{-1}, corresponding to the out-of-plane bending vibrations of ST units in the PS blocks. This result indicates that PU-PS-5 consists of PU and PS blocks.

The number-average molecular weight (M_n) of PU macromonomer was calculated by NMR, using benzaldehyde as an internal standard. The M_ns of PU macromonomer chains containing HEA groups at one end or both ends were calculated to be about 6000 and 3000, respectively. This result is in good agreement with the GPC data ($M_n \sim 4000$) (Table 2), since not all PU macromonomer chains are expected to contain HEA groups at both chain ends. Furthermore, the GPC measurements cannot give very accurate M_n values of PU macromonomer since PU macromonomers and PS standards are chemically quite different. The PU and PS content in the PU-PS-5 were also calculated, using the proton NMR integrals of NH (PU macromonomer segment) and phenyl (PS block) groups. Assuming that the M_n of PU macromonomer is in the range from 3000 to 6000, the content of PU and PS blocks were calculated to be 87–79 and 13–21 wt%, respectively. Based on the recipe for PU-PS-5, the contents of PU segment and PS block are expected to be 84 and 16 wt%, respectively. Thus the two different data are in good agreement within the experimental errors.

The dried polymer films, prepared from of the emulsions, were immersed in toluene to dissolve any PS homopolymers, but there was nothing left in the containers when the films were removed and toluene was evaporated. This result, along with the ^{1}H NMR and FT-IR spectral data, indicated that PS homopolymers were not formed in an appreciable amount, but PU–PS copolymers were formed. The copolymer films were completely dissolved in chloroform, indicating that the copolymers were not efficiently cross-linked even though the HEA end-capped PU macromonomers were used.

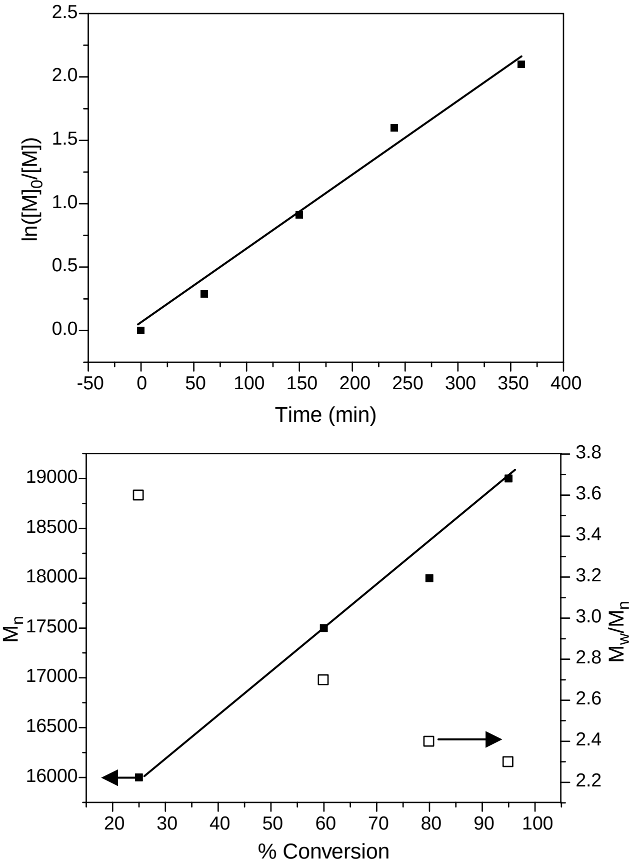
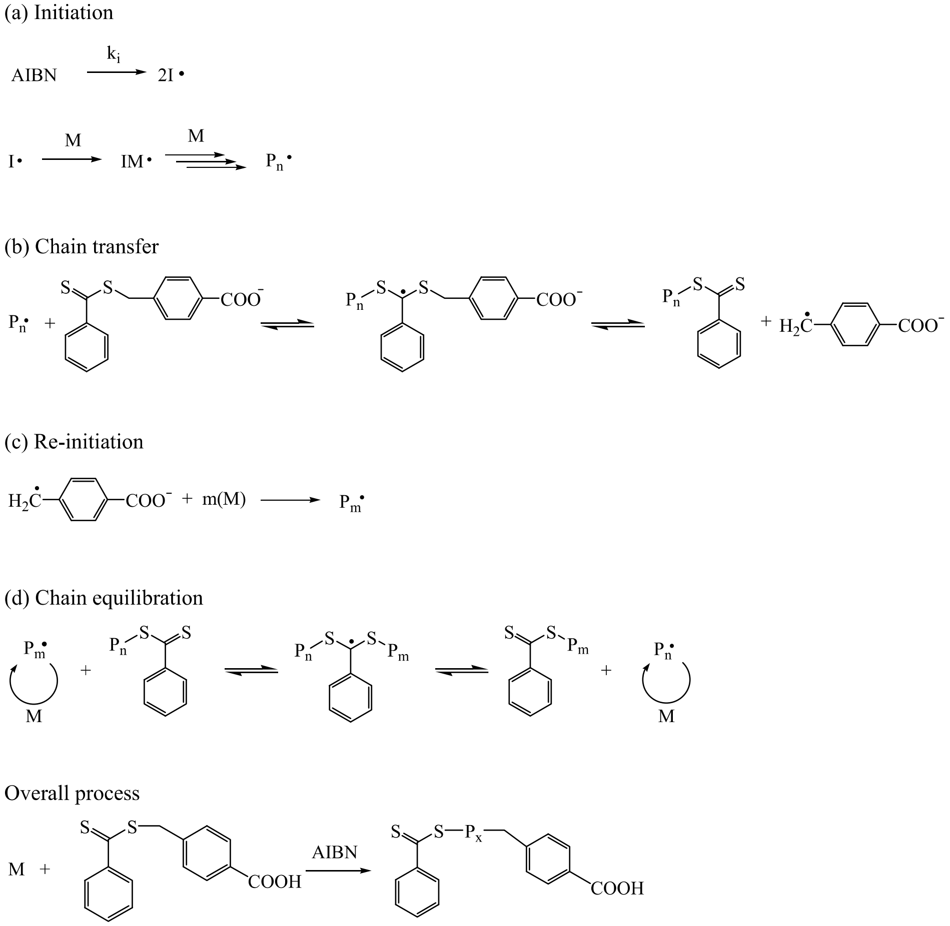


Fig. 3. (a) Pseudo-first-order kinetic plot and (b) dependence of M_n and polydispersity ($=M_w/M_n$) on the conversion in the emulsion polymerization of PU macromonomer and ST for the formation of PU-PS-5 (BTMBA/AIBN = 5/1).

A living polymerization may be characterized by linear increase in molecular weight but decrease in the molecular weight distribution with conversion. Some aliquots were withdrawn at predetermined time intervals for GPC analysis during polymerization for the preparation of PU-PS-5 (Table 2). The plots of the GPC data are shown in Fig. 3. The number-averaged molecular weight (M_n) of PU-PS-5 increased linearly with conversion, while the PDI value decreased. When the molar ratio was increased from 0 to 5, the PDI value gradually decreased and approached to that of PU macromonomers. This result indicates that molecular weight of PU–PS copolymers became more uniform, due to the more efficient RAFT process at higher molar ratio of BTMBA to AIBN. These results indicate that polymerization of ST and HEA end-capped PU macromonomer followed a living mechanism in the presence of the RAFT agent and AIBN. The mechanism by which the process imparts living character to the polymerization is shown in Scheme 2, as proposed in the literature [16]. First, the RAFT agent is consumed by propagating radicals by an addition–fragmentation mechanism. Then the fragmented radical reinitiates polymerization, resulting in new propagating radicals which then take part in the equilibrium established between the dormant polymer and



Scheme 2. Proposed mechanism of the RAFT polymerization process, where M and P (P_m, P_n and P_x) denote monomer (PU macromonomer PU and ST) and polymer chain, respectively.

active chains. The equilibration process allows all chains produced to grow in a uniform manner.

To reveal that the polymerization via RAFT process followed a living mechanism, a certain amount of ST monomer was added to PU-PS-5, and the post polymerization was allowed to occur at 60 °C for 6 h, without adding any initiators. The GPC data indicated that the M_n (44,000) of resulting polymer (PU-PS-5-PS) was larger than that (19,000) of PU-PS-5. The theoretical molecular weight, $M_{n,th}$ of PU-PS-5-PS was calculated via the following equation:

$$M_{n,th} = \left(\frac{[ST]_0 MW_{ST}}{[PU-PS-5]_0}\right)\rho + MW_{PU-PS-5}$$

Here $[ST]_0$, MW_{ST}, $[PU\text{-}PS\text{-}5]_0$, ρ, and $MW_{PU\text{-}PS\text{-}5}$ represent the initial ST concentration, molecular weight of ST, initial concentration of PU-PS-5, conversion based added ST, and the molecular weight of PU-PS-5, respectively [16]. The $M_{n,th}$ was calculated to be 46,000, which is very close to the experimental value (M_n 44,000). This result indicates that the polymerization of ST and PU macromonomers proceeded via the living mechanism in the presence of the RAFT agent and AIBN.

The average sizes of the emulsion droplets are shown in Table 2. The size distribution of the emulsion droplets also became gradually narrower as the molar ratio of BTMBA to AIBN was increased from 0 to 5 (data not shown). In fact, the copolymer emulsions, prepared via the RAFT process, appeared slightly bluish. This indicates that the copolymers became more negatively charged as the molar ratio of the

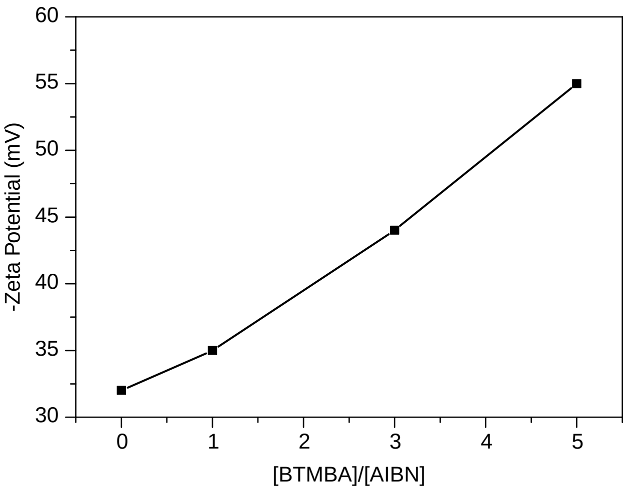


Fig. 4. Zeta potentials of PU–PS copolymer emulsions prepared by polymerization of PU macromonomer and ST in the presence of various ratios of BTMBA to AIBN, where the ratios were 0, 1, 3, and 5, to prepare PU-PS-0, PU-PS-1, PU-PS-3, and PU-PS-5, respectively.

Table 3
Tensile property, hardness and water absorption of PU–PS copolymer and PUD films

Sample code	Tensile strength (N/mm^2)	Young's modulus (N/cm^2)	Elongation at break (%)	Hardness (shore A)	Water absorption R (%)
PU-PS-0	11	830	200	92	16
PU-PS-1	13	1390	160	91	18
PU-PS-3	14	1410	170	90	14
PU-PS-5	16	1320	180	93	15
PUD	2	210	690	68	28

RAFT agent to AIBN increased. It is known that the highly developed charge on the surface of particles gives rise to a decrease in the size of the particles. The current experimental results are important in terms of demonstrating the stability of PU–PS hybrid emulsions, since the incorporation of carboxyl group-containing RAFT agent into polymer chains can significantly enhance in the storage stability of the resulting polymer emulsions.

The zeta potentials are important data because they are indicative of emulsion stability [18]. The greater magnitude of the zeta potential endows the colloid system with improved stability against coagulation. Fig. 4 shows that the zeta potential of the emulsions increased as the molar ratio of BTMBA to AIBN increased while all other polymerization parameters were kept the same. This result indicates that the stability of the emulsions can be enhanced through the incorporation of the RAFT agent into the copolymer system. This result is consistent with the average size and size distribution of the emulsion droplets, which decreased as the molar ratio of BTMBA to AIBN increased. During the storage of the copolymer emulsions at ambient temperature, no precipitation was observed for longer than 6 months. This result suggests that the copolymer emulsions prepared employing the RAFT process may exhibit enhanced storage stability, relative to the emulsions prepared by the conventional free radical polymerization method.

The glass transition (T_{g1}) and melting temperature (T_m) of PUD were measured to be −76 and 23 °C, respectively, which correspond to the phase transition temperatures of soft segments of PU chains in the PUD. On the other hand, the T_{g1} and T_m of PU–PS copolymers were measured to be in the range of −77 to −74 and 24–26 °C, respectively. This result indicates that the thermal transitions are due to the PU component in the copolymers. There was no significant change in either of the T_{g1} and T_m values in the copolymers. This result is understandable because the copolymers were synthesized under the same conditions except for the molar ratio of BTMBA to AIBN. The T_{g2} of PS blocks in the copolymers were in the range from 98–102 °C. This result indicates that the T_{g2} values of PS blocks were not significantly changed by such different distributions of PS blocks in the copolymers.

The tensile strength and elongation at the break of the dried polymer films prepared from the emulsions are listed in Table 3. The tensile strengths of the copolymer films (11–16 N/m^2) were significantly larger than that of the PUD films (2 N/m^2). The elongations at the break of the copolymer films (180–200%) were much smaller than that of the PUD films (690%), as expected. The hardness (shore A) of the copolymer films (92–93) was greater than that of the PUD films (68), due to the presence of the PS blocks in the copolymers, which are harder than the PU blocks. The copolymer films exhibited much smaller water absorption (15–18%) than that of the PUD films (28%). This result indicates that the water-resistance of PU films can be significantly improved by incorporation of hydrophobic PS blocks into PU blocks. Overall, the copolymer films did not exhibit any significant difference in their mechanical properties. The relative amount of BTMBA employed for the preparation of PU-PS-1, PU-PS-3 and PU-PS-5 was 2, 6 and 8 wt%, respectively. This indicates that the small contents of the RAFT agent, relative to the other components, do not appreciably affect the mechanical properties of the resulting copolymer films.

4. Conclusions

The PU–PS copolymer emulsions were successfully prepared via RAFT process. The PDI value of the PU–PS copolymers was decreased as the molar ratio of BTMBA to AIBN was increased. On the other hand, as the molar ratio of BTMBA to AIBN increased, the zeta potential of the emulsions increased, but the average size and size distribution of the emulsion droplets decreased. Incorporation of PS blocks into the PU chains led to significant enhancement in tensile strength, hardness and water-resistance. Our current strategy employing the RAFT process may be very useful in preparing PU-vinyl polymer hybrid emulsions with high storage stability.

Acknowledgements

This research was supported financially by the BK-21 project in 2003.

References

[1] Madbouly SA, Otaigbe JU, Nanda AK, Wicks DA. Macromolecules 2005;38:4014.

[2] Lee D-K, Tsai H-B, Wang H-H, Tsai R-S. J Appl Polym Sci 2004;94:1723.

[3] Sundar S, Aruna P, Radhakrishnan G. Colloid Polym Sci 2004;283:209.

[4] Lee JS, Kim BK. Prog Org Coat 1995;25:311.

[5] Lu MG, Lee JY, Shim MJ, Kim SW. J Appl Polym Sci 2002;86:3461.

[6] Kim BK, Lee JC. Polymer 1996;37:469.

[7] Yuan J, Hou QF, Liu BL, Shen J, Lin SC. Colloids Surf B Biointerf 2004;36:19.

[8] Romero-Sánchez MD, Pastor-Blas MM, Martín-Martínez JM. Int J Adhes Adhes 2003;23:49.

[9] Jung JA, Kim BK. Opt Commun 2005;247:125.
[10] Hua DB, Sun W, Bai RK, Lu WQ, Pan CY. Eur Polym J 2005;41:1674.
[11] Charleux B, Nicolas J, Guerret O. Macromolecules 2005;38:5485.
[12] Xia J, Zhang X, Matyjaszewski K. Macromolecules 1999;32:4482.
[13] Charleux B, Nicolas J, Guerret O. Polymer 2004;45:7791.
[14] Smulders W, Gilbert RG, Monteiro MJ. Macromolecules 2003;36:4309.
[15] Ladavière C, Dörr N, Claverie JP. Macromolecules 2001;34:5370.
[16] Bussels Raf. (Multi)block copolymer synthesis via controlled radical polymerization in aqueous dispersions. Technische Universiteit Eindhoven; 2004.
[17] Shim SE, Shin YD, Jun JW, Lee KS, Jung HJ, Choe SJ. Macromolecules 2003;36:7994.
[18] Shim SE, Shin YD, Jun JW, Lee KS, Jung HJ, Choe SJ. Macromolecules 2004;37:5565.