

Synthesis and Characterization of Linear Waterborne Poly(ethyl acrylate-urethane) Prepared from Poly(ethyl acrylate) Diol Via Atom Transfer Radical Polymerization

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ABSTRACT: Linear waterborne poly(ethyl acrylate-urethane)s (PEA-U)s were synthesized by reacting a poly(ethyl acrylate) diol (HO-PEA-OH) with isophorone diisocyanate (IPDI) and 2,2-bis(hydroxymethyl) propionic acid (DMPA). The poly(ethyl acrylate) (HO-PEA-Br) was prepared by atom transfer radical polymerization of ethyl acrylate with a designed molecular weight (M_n) of about 2000 and the hydroxyl (OH) end capped poly(ethyl acrylate) (HO-PEA-OH) was obtained by substituting the bromo end group with *N*-ethanol methyl amine. The HO-PEA-OH of M_n 2000 with OH functionality of about 1.92 and the linear waterborne PEA-U with M_n of about 13,300 were obtained and characterized by hydrogen nuclear

magnetic resonance ($^1\text{H-NMR}$), gel permeation chromatography, thermo gravimetric analysis, and differential scanning calorimetry. When the ratio of isocyanate to hydroxyl group (NCO/OH) was 1.4 and DMPA was 5 wt %, the waterborne PEA-U was a tough material with a tensile strength of 4.9 MPa, elastic modulus of 31.9 N/mm² and elongation at break of about 286%, which showed its potential applications in many fields. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: waterborne poly(ethyl acrylate-urethane); atom transfer radical polymerization; poly(ethyl acrylate) diol; polyurethanes; telechelics

INTRODUCTION

Atom transfer radical polymerization (ATRP) is one of the most promising controlled radical polymerization (CRP) technologies and is used to synthesize telechelic polymers, especially for vinyl materials.^{1–10} Hydroxyl end capped poly(alkyl acrylate)s or poly(alkyl acrylate) diols are especially of interest because of their potential applications in coatings, adhesives, polyurethanes, and other fields. Linear or branched hydroxyl end capped poly(alkyl acrylate)s were prepared by ATRP polymerization of alkyl acrylate followed by end group substitution by alkylol amine or other technologies.^{6, 11–14} However, few reports appeared on the further applications of these telechelic polymers. New materials could be further developed and investigated from these poly(alkyl acrylate) diols or other telechelic poly(alkyl acrylate)s prepared from ATRP. Conversely, poly(alkyl acrylate-urethane)s are important in coating and adhesive fields because they combine both merits of polyacrylate and polyurethane materials. Typical methods of preparing the copolymers of alkyl acry-

late-urethane include the emulsion copolymerization, interpenetrating network technologies, and photopolymerizations, and so on. However, the poly(alkyl acrylate-urethane)s prepared by these methods have the structure of three dimensional network or the poly(alkyl acrylate)s and polyurethanes are connected by interchain networks. The long alkyl acrylate segments are not incorporated into the main chain of the copolymer and linear poly(alkyl acrylate-urethane)s are difficult to be synthesized by these methods. Combination of ATRP or other CRPs and polycondensation technologies makes it possible to synthesize novel linear copolymers of alkyl acrylate and urethane, styrene, and urethane,^{15–20} which may show great potential applications in many industrial fields.

In our previous research, we have successfully synthesized poly(butyl acrylate) diol with a designed molecular weight of 2000 using ATRP polymerization of butyl acrylate, followed by nucleophilic substitution of the bromo end group with *N*-ethanol methyl amine.²¹ In this article, we tried to synthesize and characterize a new kind of linear waterborne poly(ethyl acrylate-urethane) (PEA-U) by reacting the poly(ethyl acrylate) diol (HO-PEA-OH), which was synthesized through ATRP of ethyl acrylate (EA), with isophorone diisocyanate (IPDI) and 2,2-bis(hydroxymethyl) propionic acid (DMPA).

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EXPERIMENTAL

Materials

Analytic grade EA, pentmethyl diethylene triamine (PMDETA), *N*-methyl ethanol amine, IPDI, 2,2-bis(hydroxymethyl)propionic acid (DMPA) and other chemicals were commercially available from Sino-pharm Chemical Reagent Co. (Shanghai, China) and used as received unless otherwise stated. Analytic grade copper(I) bromide (CuBr) was commercially available and purified by washing with acetic acid before use. 4-Hydroxybutyl 2-bromo-*iso*-butyrate was synthesized according to the literature.²¹

Synthesis of poly(ethyl acrylate) (HO-PEA-Br) with designed M_n of 2000

To a four-necked flask equipped with a magnetic stirrer, thermometer, and rubber stoppers were added EA 102.5 g (1.025 mol), 4-hydroxybutyl 2-bromo-*iso*-butyrate 13 g (0.0506 mol, purity: 95%), CuBr 1.00 g (0.0069 mol), PMDETA 2.4 g (0.0139 mol), toluene 25 mL. The mixture was degassed three times and the reaction was then kept under N₂ at 60°C for about 8 h. Deep green viscous product was obtained before purification. After the product was columned with silica gel to remove the catalysts, a light yellow viscous product was obtained. Yield: 96% (110 g). The degree of polymerization of the PEA-Br was designed to be 20.25, controlled by the molar ratio of monomer (EA) to initiator and the M_n was controlled to be about 2025.

Synthesis of HO-PEA-OH with designed M_n of 2000

To a four-necked flask equipped with a magnetic stirrer, thermometer, and rubber stoppers were added HO-PEA-Br 110 g ($M_n = 2000$; Br: 0.055 mol), *N*-methyl ethanol amine 103.9 g (1.39 mol) and triethylamine 30 g (0.297 mol). The mixture was degassed three times and the reaction was then kept under N₂ at 90°C for 24 h. After that, the reaction mixture was dissolved in ethyl acetate and the ethyl acetate solution was first washed with 5% diluted hydrochloric acid solution and then with saturated sodium chloride solution until pH reached 7 to remove the excess *N*-methyl ethanol amine. Then, the solution was passed through a column filled with basic aluminum oxide to remove the *N*-methyl ethanol amine residue. The solution was dried with magnesium sulfate and the solvent was removed through rotary evaporator. After dried under vacuum, a yellow viscous product was obtained. Yield: 43.8% (48.5 g).

Synthesis of waterborne PEA-U

Two kinds of PEA-U were prepared which had the molar ratio of isocyanate to hydroxyl group (NCO/

OH) 1.1 and 1.4, respectively. To a four-necked flask equipped with a magnetic stirrer, thermometer and rubber stoppers were added with DMPA, IPDI, dibutyltin dilaurate, and ethyl methyl ketone. The amount of DMPA used was 5 wt % to the weight of monomers. The mixture was kept at 70°C for about 2 h. Then, the HO-PEA-OHs were added to the reaction mixture and the reaction was kept at 75°C for another 4 h. After the mixture was cooled down to room temperature, triethylamine, and acetone were added. After being stirred for about 10 min, the reaction mixture was poured to water and stirred for about 5 h for chain extension to obtain a linear waterborne PEA-U. The solid content of the emulsion was controlled to be about 20%. The polyether type waterborne polyurethane (PPG-U) was prepared using the same procedure except the poly(propylene glycol) (PPG) with M_n of 2000 was used as a diol.

Characterization

Hydrogen nuclear magnetic resonance (¹H-NMR) spectra were recorded using Bruker DMX 500 MHz spectrometer, deuteriochloroform as a solvent, and tetramethylsilane as an internal standard. Gel permeation chromatography (GPC) of polymers were measured with Waters 1515, tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min, polystyrene as a standard, to get molecular weights and polydispersities of polymers. Thermo gravimetric analysis (TGA) was performed on SDT Q600 from TA instrument under nitrogen and at the rate of 20°C/min. The glass transition temperature (T_g) of the polymers were measured using Pyris 1 differential scanning calorimetry (DSC) of Perkin Elmer at the rate of 20°C/min, under nitrogen atmosphere. The mechanical properties of waterborne PEA-U films were measured according to the standard of GB/T1040-92, China. The PEA-U films were prepared by casting the PEA-U emulsions on PET sheets and dried at room temperature for about 1 week, and then, the resulting polymer films were dried in vacuum oven at 60°C overnight.

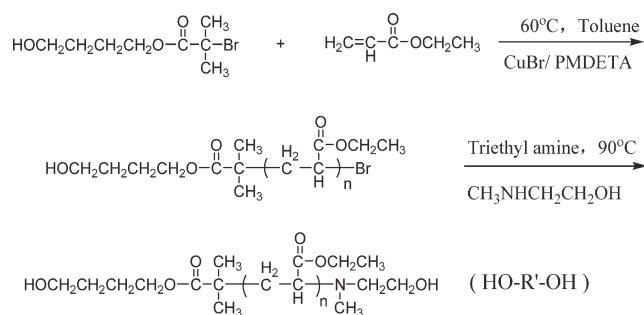
RESULTS AND DISCUSSION

Reaction scheme of synthesizing waterborne PEA-U_s

The reaction schemes of synthesizing HO-PEA-OH and linear waterborne PEA-U_s were shown in Schemes 1 and 2, respectively.

Synthesis and characterization of HO-PEA-OH

The HO-PEA-OH was synthesized using ATRP of EA followed by the substitution of bromo end group with *N*-methyl ethanol amine, as shown in Scheme 1. Figure 1 shows the kinetic plot and the plot of



Scheme 1 Reaction scheme of synthesizing HO-PEA-OH via ATRP.

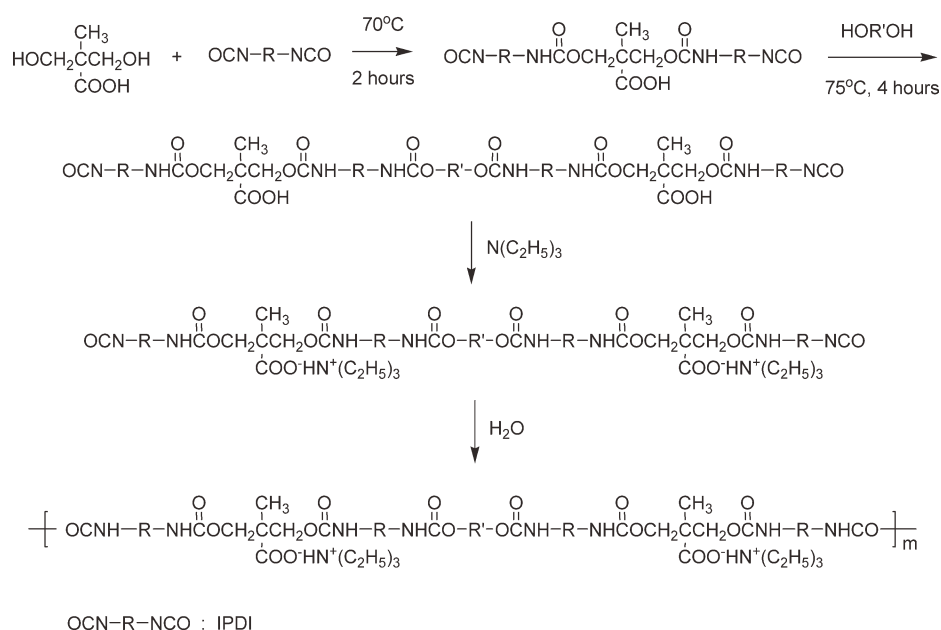
molecular weights and molecular distributions changes with monomer conversion. The linear relationship between $\ln([M]_0/[M])$ and reaction time, which could be obtained from Figure 1(a), indicates that the polymerization of EA was in a typical living polymerization. The molecular weights increased gradually with conversion and the PDI was near 1.20, as seen from Figure 1(b). Figure 2 shows the $^1\text{H-NMR}$ spectrum of poly(ethyl acrylate) (HO-PEA-Br) with designed molecular weight of about 2000. The typical chemical shifts of the protons are indicated in the Figure 2. The molecular weight of poly(ethyl acrylate) can be estimated from the relative integration area ratio of proton *b* to *a* in this NMR spectrum, $M_n = [(2 \times 8.27)/1.00] \times 100 + 140 = 1794$, which is in good agreement with the designed molecular weight.

Figure 3 shows the $^1\text{H-NMR}$ spectrum of HO-PEA-OH. The peaks of the protons from *N*-methyl ethanol amine segment at the end of PEA are indicated in this figure. The OH functionality of the HO-

PEA-OH can be estimated from this spectrum. The relative ratio of the integration area of peak *d* to that of peak *c* is about 0.92, which means that the overall functionality of OH of the HO-PEA-OH was about 1.92, because the initiator already has an OH group. It seemed difficult to get the functionality as high as 2.0 by the end group substitution. One of the reasons is that reactivity of the bromo end group on a polymer chain is relatively low compared with that of low molecular weight compound and it is hard to get 100% conversion by substitution. The other reason is that some bimolecular termination still occurred in ATRP,²² which means that not all the poly(ethyl acrylate) chain has a bromo end group. The molecular weight of the HO-PEA-OH can also be estimated from this $^1\text{H-NMR}$ spectrum by the relative integration ratio of peak *b* to peak *a*, $M_n = [(2 \times 8.01)/1.00] \times 100 + 140 + 74 = 1816$, which is in good accordance with that of HO-PEA-Br.

Synthesis and characterization of linear waterborne PEA-U

Scheme 2 shows the synthetic route of linear waterborne PEA-U. When the content of DMPA was more than 5 wt %, a stable PEA-U emulsion was obtained and the size of the emulsion droplet was below 100 nm. Table I shows the molecular weights of waterborne PEA-U, high molecular weight of about M_n 13,300 and PDI of about 4.02 were obtained. The broad molecular weight distribution of the PEA-U may be due to the low functionality of HO-PEA-OH which was less than 2 and the bad control of the chain extending process. Also, a slight broader molecular weight distribution of HO-PEA-OH was



Scheme 2 Reaction scheme of synthesizing linear waterborne PEA-U.

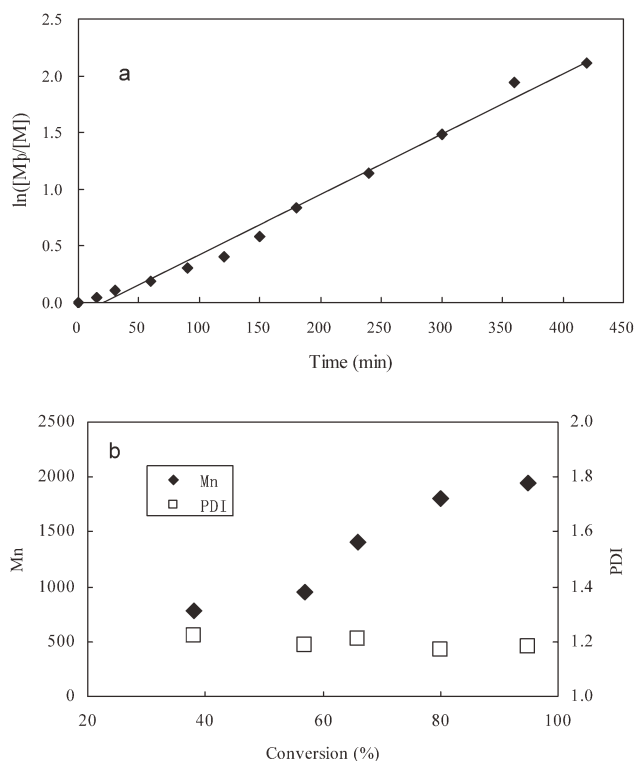


Figure 1 (a) Kinetic plot of ATRP of EA. (b) Molecular weights and molecular weight distributions versus conversion.

obtained compared with that of HO-PEA-Br, which may be caused by the possible side reactions during the bromo substitution.

Figure 4 shows the IR spectra of HO-PEA-Br, HO-PEA-OH, and PEA-U. Comparing the IR spectra of HO-PEA-Br and HO-PEA-OH, it could be found that the relative intensity of OH absorption peak at around 3500 cm^{-1} became stronger for HO-PEA-OH, indicating more OH groups in HO-PEA-OH than that in HO-PEA-Br. The peak at around 1640 cm^{-1} , which was attributed to C—N vibration absorption,

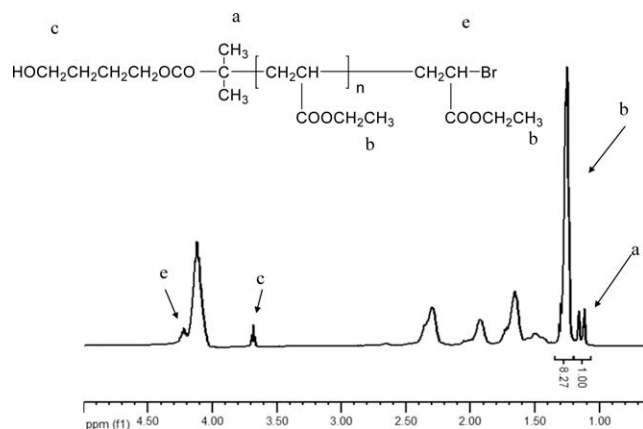


Figure 2 $^1\text{H-NMR}$ spectrum of poly(ethyl acrylate) (HO-PEA-Br) prepared by ATRP.

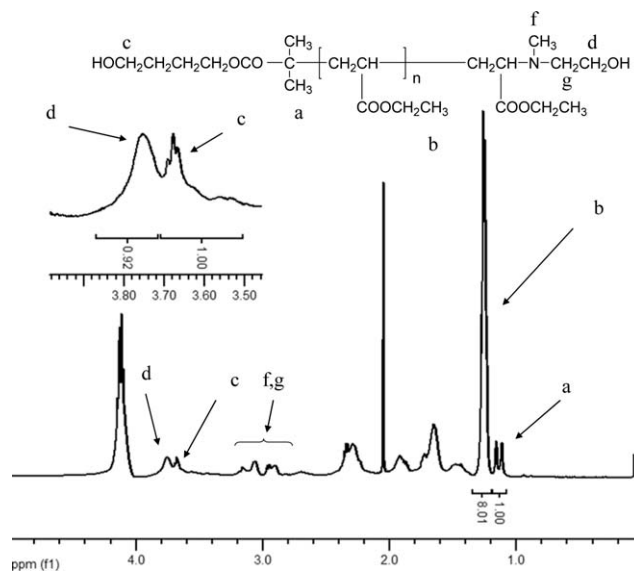


Figure 3 $^1\text{H-NMR}$ spectrum of HO-PEA-OH.

appeared for both HO-PEA-OH and PEA-U compared with that of HO-PEA-Br, indicating C—N bonds exist in these two polymers. In IR spectrum of PEA-U, relative intensity of this peak became stronger than that of HO-PEA-OH due to more C—N bonds in the PEA-U.

Figure 5 shows the DSC curves of HO-PEA-OH and PEA-U. The glass transition temperature (T_g) of HO-PEA-OH was about -23.6°C , while the T_g of PEA-U with NCO/OH of 1.1 was about 19.1°C and the T_g for PEA-U with NCO/OH of 1.4 was about 23.1°C , respectively. The higher T_g for PEA-U than that of PEA is due to the higher molecular weight of PEA-U and the rigid urethane segment in PEA-U main chain which increases the interaction between polymer chains. More rigid urethane segment gave higher T_g , which can be obtained by comparing the T_g s of PEA-U with NCO/OH of 1.1 and 1.4.

Figure 6 shows the TGA curves of poly(ethyl acrylate) with bromo end group (HO-PEA-Br), HO-PEA-OH, and PEA-U. Because of the instability of the bromo end group, the HO-PEA-Br showed a lower initial decomposition temperature than that of HO-PEA-OH, which also indicated that the nucleophilic substitution of bromo end group with *N*-methyl monoethanol amine was successful. The waterborne PEA-U TGA curve showed three decomposition

TABLE I
Molecular Weights of Poly(ethyl acrylate-urethane) by GPC

Polymers	M_n	M_w	PDI
HO-PEA-Br	2200	2500	1.16
HO-PEA-OH	2500	3300	1.32
PEA-U	13,300	53,500	4.02

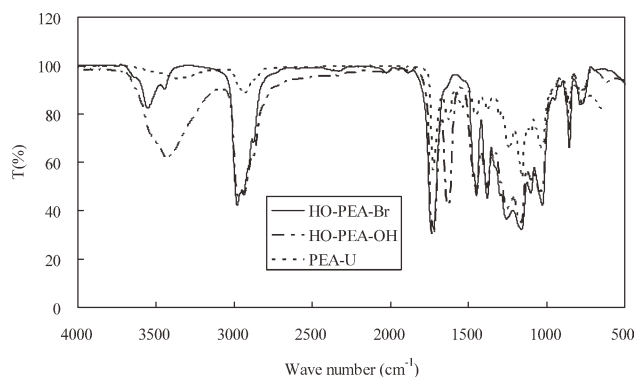


Figure 4 IR spectra of HO-PEA-Br, HO-PEA-OH, and PEA-U.

temperatures, 204, 287, and 395°C, respectively. It was believed that triethyl ammonium salt was decomposed at around 204°C, and the decomposition temperature of 287°C was attributed to the decomposition of urethane segment and the poly(ethyl acrylate) segment decomposed at about 395°C.

Figure 7 gives the strain–stress curve of PEA-U (PEA-U 1.4). The tensile strength of PEA-U was about 4.9 MPa, the elastic modulus was 31.9 N/mm² and elongation at break was 286%. And the polyether type waterborne polyurethane (PPG-U) prepared from PPG with M_n of 2000 and the NCO/OH ratio of 1.4 had the tensile strength of about 1.31 MPa, the elastic modulus of about 0.4 N/mm² and the elongation at break of about 559%. The differences between the mechanical properties of these two materials suggest that poly(ethyl acrylate) was a more rigid chain segment than the PPG, and provided the polyurethane with a higher tensile strength and lower elongation at break. The results showed that the waterborne PEA-U was a hard and tough material which may find applications in various fields, such as coatings, adhesives, and elastomers.²³

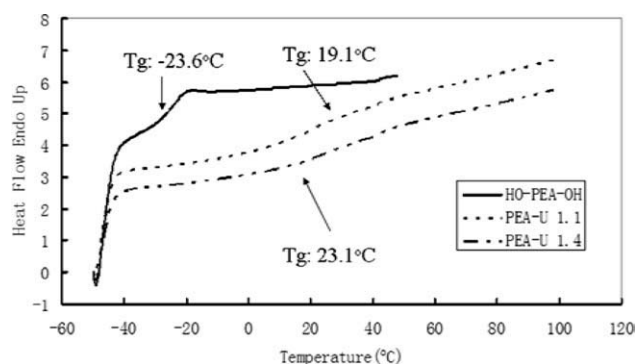


Figure 5 DSC curves of HO-PEA-OH and PEA-U.

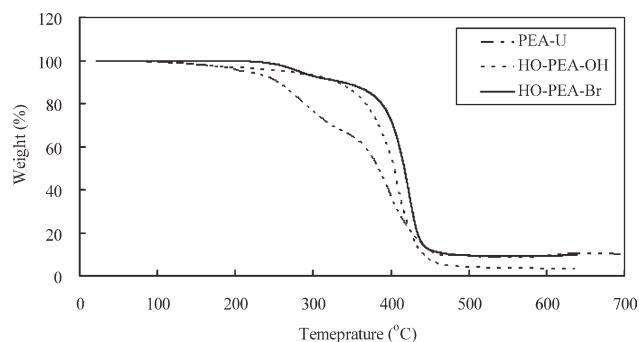


Figure 6 TGA curves of HO-PEA-Br, HO-PEA-OH, and PEA-U.

CONCLUSIONS

Linear aqueous PEA-U copolymers were synthesized using ATRP and polycondensation techniques. HO-PEA-OH with M_n of about 2000 and OH functionality of about 1.92 was successfully synthesized by using ATRP of EA followed by nucleophilic substitution of bromo end group with *N*-methyl ethanol amine. The structure of HO-PEA-OH with M_n of 2000 was confirmed by the ¹H-NMR spectrum, GPC, and TGA. A linear waterborne PEA-U with M_n of about 13,300 was then obtained by reacting the HO-PEA-OH with IPDI and 2,2-bis(hydroxymethyl) propionic acid (DMPA). Because of the high molecular weight and rigid urethane segment, the waterborne PEA-U showed higher T_g than that of HO-PEA-OH. When the NCO/OH ratio was controlled to be about 1.4, the waterborne PEA-U had a tensile strength of about 4.9 MPa, elastic modulus of about 31.9 N/mm² and elongation at break of about 286%, which showed a higher tensile strength and lower elongation at break than those of PPG type waterborne polyurethane.

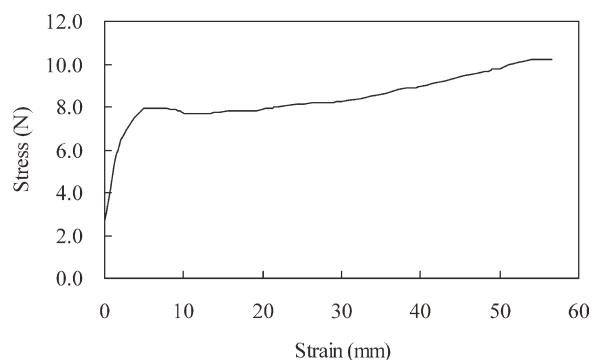


Figure 7 Stress–strain curve of linear waterborne PEA-U (NCO/OH: 1.4).

References

1. Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921.
2. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
3. Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
4. Wade, A. B.; Matyjaszewski, K. *J Mol Catal A Chem* 2006, 254, 155.
5. Blazquez, J. A.; Areizaga, J.; Iruin, J. J.; Miguel, O.; Mecerreyes, D.; Jounanneau, J. *React Funct Polym* 2006, 66, 1073.
6. Zhang, H. Q.; Jiang, X. L.; Linde, R. V. D. *Polymer* 2004, 45, 1455.
7. Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog Polym Sci* 2001, 26, 337.
8. Siegwart, D. J.; Oh, J. K.; Gao, H. F.; Bencherif, S. A.; Perineau, F.; Bohaty, A. K.; Hollinger, J. O.; Matyjaszewski, K. *Macromol Chem Phys* 2008, 209, 2179.
9. Popescu, D.; Keul, H.; Moeller, M. *Macromol Chem Phys* 2008, 209, 2012.
10. Matyjaszewski, K.; Nakagawa, Y.; Gaynor, S. G. *Macromol Rapid Commun* 1997, 18, 1057.
11. Coessens, V.; Nakagawa, Y.; Matyjaszewski, K. *Polym Bull* 1998, 40, 135.
12. Coessens, V.; Matyjaszewski, K. *Macromol Rapid Commun* 1999, 20, 127.
13. Sarbu, T.; Lin, K. Y.; Spanswick, J.; Gil, R. R.; Siegwart, D. J.; Matyjaszewski, K. *Macromolecules* 2004, 37, 9694.
14. Lutz, J. F.; Boerner, H. G.; Weichenhan, K. *Macromol Rapid Commun* 2005, 26, 514.
15. Hemant, V.; Kannan, T. *Polym Int* 2007, 57, 226.
16. Hemant, V.; Kannan, T. *J Macromol Sci Part A* 2009, 46, 179.
17. Jin, Y. Z.; Hahn, Y. B.; Nahm, K. S.; Lee, Y. S. *Polymer* 2005, 46, 11294.
18. Ibarboure, E.; Baron, A.; Papon, E.; Rodriguez-Hernandez, J. *Thin Solid Films* 2009, 517, 3281.
19. Nayak, S.; Hemant, V. H.; Kannan, T. *Colloid Polym Sci* 2010, 288, 181.
20. Radhakrishnan, B.; Chambon, P.; Cloutet, E.; Cramail, H. *Colloid Polym Sci* 2003, 281, 516.
21. Li, J.; Sun, Z. D.; Zhen, Y. P.; Ren, Q.; Yu, Q.; Cui, Y.; Yamagishi, M.; Ikeda, Y. *J Polym Res* 2010, 17:551.
22. Tang, W.; Tsarevsky, N. V.; Matyjaszewski, K. *J Am Chem Soc* 2006, 128, 1598.
23. Guyot, A.; Landfester, K.; Schork, F. J.; Wang, C. P. *Prog Polym Sci* 2007, 32, 1439.