Synthesis, Characterization, and Pressure-Sensitive Properties of Butyl Acrylate and Methyl Acrylate Copolymers

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ABSTRACT: Butyl acrylate and methyl acrylate copolymers were prepared and evaluated as pressure-sensitive adhesives. The effects of polymerization conditions such as the temperature, time, amounts of the monomers, and feeding method on the molecular weight, molecular weight distribution, and composition of the resultant copolymers were investigated. The adhesive properties were evaluated in terms of the viscosity, peel strength, and hold time. The best molar ratio of methyl acrylate in the copolymer was 0.466 for pressure-sensitive adhesives. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1535–1542, 2006

Key words: acrylate copolymer; pressure-sensitive adhesive; adhesive character; reactivity ratios

INTRODUCTION

Pressure-sensitive adhesives (PSAs) are designed to stick on almost any surface by simple contact under light pressure. They do not undergo any physical transformation or chemical reaction during the bonding process,[1,2] Therefore, the rheological properties of the adhesives must be finely tuned for the application, combining a discreetly chosen polymer architecture and monomer composition in the polymer. Because of their excellent properties, including aging resistance and light stability, acrylate copolymers have gained considerable significance over other various polymers.

The copolymer of butyl acrylate (BA) and methyl acrylate (MA) was synthesized early on and used for PSAs. Courtaulds, Ltd.,[3] prepared the copolymer in a solvent in the presence of 2,2'-azodiisobutyronitrile (AIBN) as an initiator. Then, de Meulemeester[4] investigated the self-adhesive character of poly(methyl acrylate-*co*-butyl acrylate) [poly(MA-*co*-BA)] and got an excellent kind of PSA by adding proper tackifying resins. Quach and Otsu[5] prepared head-to-tail polymers of MA with BA and found that the glass-transition temperatures of the head-to-head polymers were somewhat higher than those of the corresponding head-to-tail copolymers; this indicated lower chain flexibility in the former. Haken and McKay[6] first studied poly(MA-*co*-BA) with a Curie point pyrolysis system and developed a method for distinguishing between the copolymers and their homopolymer mixtures. Poly(MA-*co*-BA) was also analyzed and compared with corresponding homopolymer blends.

However, until now, our understanding of the composition, structure, and properties of poly(MA-*co*-BA) PSAs and, in particular, the specific roles of the different components in poly(MA-*co*-BA) PSAs was still very limited. In this study, BA and MA copolymers were prepared and characterized. The reactivity ratios of MA and BA were calculated with the Kelen–Tudos method.[7] Under the technological conditions of our experiment, no report about the influence of the reaction conditions had been presented. The effects of different reaction conditions, such as the initiator feeding method, reaction time, temperature, solvent feeding method, and molar fraction of the monomer in the copolymer, on its properties are discussed.

EXPERIMENTAL

Materials

BA (Shanghai Wulian Chemical Co., Ltd., Shanghai, China) and MA (Shanghai Wulian Chemical) were washed with 5 wt % NaOH solutions to remove the polymerization inhibitor. The initiator AIBN (Shanghai No. 4 Reagent & H. V. Chemical Co., Ltd., Shanghai, China) was recrystallized twice before use. Toluene and ethyl acetate (EA; Hangzhou Shuanglin Chemical Co., Ltd., Hangzhou, China) were used as received.
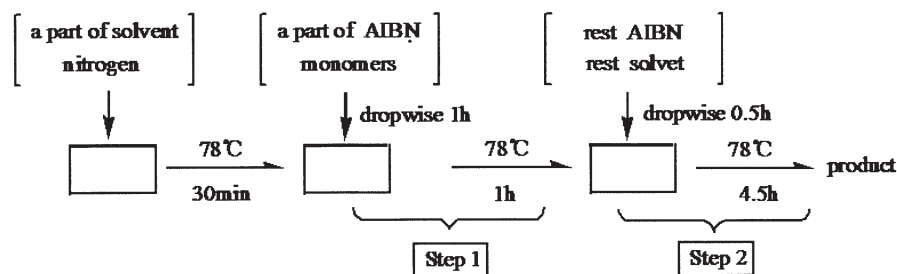
Scheme 1 Reaction process.

Synthesis

The preparation of poly(*n*-butyl acrylate-*co*-methyl acrylate) was carried out in a 250-mL, four-necked, round-bottom flask immersed in a constant-temperature oil bath at different temperatures and equipped with a reflux condenser, an efficient stirrer rotating at 120 rad/min, one dropping funnel, and a nitrogen inlet. First, some of the solvent was poured into the flask in a nitrogen atmosphere half an hour before the polymerization. Then, some of the initiator was mixed with the monomers and added dropwise over a period of 1 h. After 2 h of polymerization, the remaining initiator and solvent were mixed and added dropwise over a period of 0.5 h. The reaction proceeded continuously for another 4.5 h. The reaction process is shown in Scheme 1.

The conversion calculation method was as follows:

$$\text{Overall conversion} = \frac{W_t}{\sum M_0} \times 100\%$$

where W_t is the mass of the copolymer after drying in vacuo at 50°C for 24 h and $\sum M_0$ is the mass of the initial monomer fraction.

Characterization and measurement

Molecular weight and molecular weight distribution (MWD)

The molecular weight and MWD were tested with a Water I525/2414 gel permeation chromatograph with a laser scattering detector and Ultrastyragel columns with pore sizes of 103–105 Å. The eluent was tetrahydrofuran at a flow rate of 1.0 mL/min. A detection wavelength of 632.8 nm and a refraction-index increment of the polymer solutions of 0.20 were used for laser scattering detection.

¹H-NMR spectra

¹H-NMR spectra of the polymers were recorded with an Advance DMX500 500-MHz NMR spectrometer in CDCl₃ with tetramethylsilane as the standard.

Viscosity

The viscosities of the solutions containing the resultant copolymers were measured at room temperature (30°C) with a Hakke VT550 viscometer (GEM) (Germany) with an NV rotor.

Peel test

The peel strength of the PSA films at an angle of 180° was measured with a Zwick universal material testing machine (Italy) at 25°C at a peel rate of 100 mm/min. We used 1Cr13 stainless steel as a substrate and coated the copolymer with it to a thickness of 50 um and a width of 25 mm. Then, the Knitgoods CF05 film (China) was stuck to the substrate. The peel strength is defined as follows:

$$\text{Peel strength (KN/m)} = F/b$$

where F is the peeling force and b is the width of the strip, which serves as a measure of the peel strength.
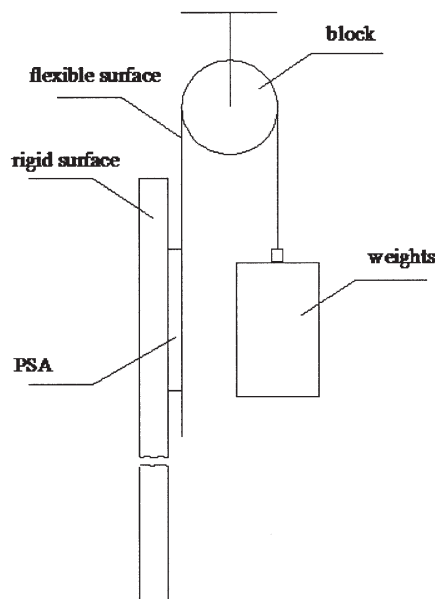

Figure 1 Hold-character testing instrument.

Sample	BA (1×10^{-3} mol/mL)		MA (1×10^{-3} mol/mL)		AIBN (1×10^{-5} mol/mL)		M_n	M_w	MP[a]	MWD
	Step 1	Step 2	Step 1	Step 2	Step 1	Step 2				
1	2.61	2.07	1.30	1.04	1.13	1.34	28,288	62,589	81,542	2.21
2	2.61	2.07	1.30	1.04	1.69	1.34	25,957	60,368	82,400	2.33

Reaction conditions: temperature = 80°C; atmosphere = nitrogen; feed method = batchwise; solvent = toluene.
[a] MP, max value of molecular weight.

Holding power

The hold character of the PSA films was measured with the equipment[8] shown in Figure 1. We performed a hold test at room temperature (24°C) after the sample was stuck to Knitgoods CF05 film (bonding area = 25 mm × 25 mm).

RESULTS AND DISCUSSION

Effect of the initiator feeding method on the molecular weight of the copolymer

With the same input amount of the initiator, the different feeding methods changed the copolymer molecular and MWD. Table I shows the details. The same input amount ensured that the changes in the properties were not caused for the following two reasons: (1) the system viscosity was lowered by the input of the solvent and so the conversion rate rose and (2) chain-transfer action was caused by the solvent and made the molecular chain length longer and homogeneous. The same main bulk of the initiator eliminated the effects of the properties by the initiator being input at the end of the reaction.

When the reaction came to the autoacceleration stage, the activity of the free radical was constrained, and the conversion rate rose slowly. Therefore, feeding the rest of the initiator could revive the monomers and molecular chains, and this made the conversion rate rise and the polymerization degree increase. As shown in Table I, the number-average molecular weight (M_n) changed from 25,957 to 28,288, and the MWD changed from 2.33 to 2.21.

The branching site during the polymerization reaction was considered, and this was attributed to chain transfer to the polymer via hydrogen abstraction from a tertiary backbone C—H bond, as shown in Scheme 2.

However, the different feeding methods of the initiator did not change the branch degree of the copolymer as we predicted. Using gel permeation chromatography, we determined the relationship between the molecular weight and elution volume. Figure 2 shows a likely U-shaped curve rather than the expected linear decrease in the molecular weight with increasing elution volume. Although the exact reasons for this abnormal behavior are unknown,[9-12] it could indicate that the copolymers had a high branching degree, and the initiator feed method did not affect it.

Effect of the reaction time on the molecular character of the copolymer

At the early stage of 78°C, the rate of conversion rose slowly; when the autoacceleration stage at 78°C was reached in about 45 ± 5 min, the reaction released heat sharply. Ten minutes later, the rate of conversion rose to 65 ± 3% and reached 95 ± 3% in 1 h more. When the reaction time was more than 7 h, the conversion changed so slowly that 7 h might have been the suitable time, as shown in Figure 3.

The molecular weight and MWD also changed with the reaction time, and in turn so did the overall conversion. Table II shows the details. The decrease in the molecular weight from 175,948 to 98,199 and the increased in MWD from 1.79 to 3.26 could be attributed to the low-molecular-weight polymers that formed at the end of the reaction as a result of the low remaining monomer concentration. On the other hand, the larger branched molecules coeluted with normally eluting smaller, linear molecules in the region of high elution

Scheme 2 Proposed branching site during the polymerization reaction. R represents the aliphatic portion of BA or MA. The long chains represent the polymer already formed.
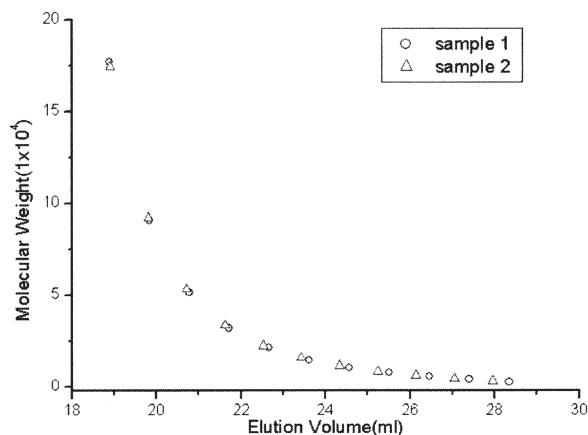
Figure 2 Elution behavior of the polymer molecules as a function of the initiator feed method.

Figure 4 Elution behavior of the polymer molecules as a function of the full reaction time. Results for 1, 2.5, and 5 h are presented.

volumes; this may also justify the results. As shown in Figure 4, the increase in the degree of the curve indicated a higher branch degree.
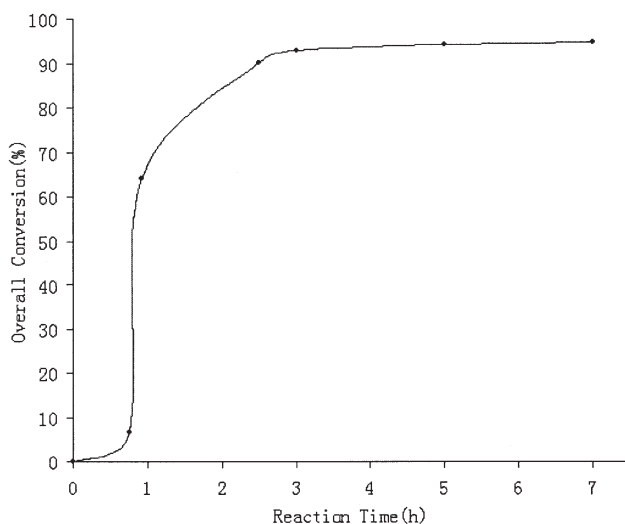

Figure 3 Relationship between the conversion ratio and time (all the copolymers were prepared under the following conditions: 80°C, nitrogen atmosphere, batchwise feed, same monomer ratios, EA as the solvent, and termination with methanol).
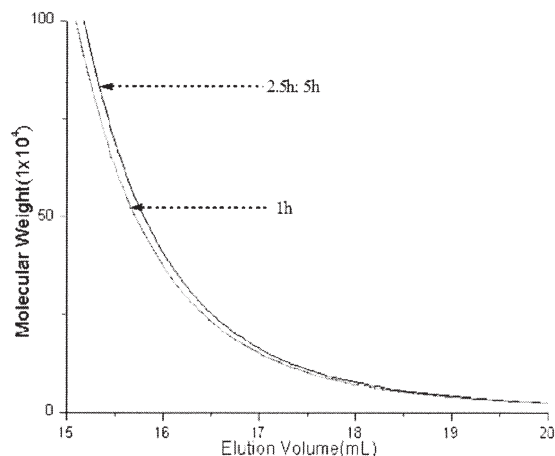
Effect of the reaction temperature on the molecular character of the copolymer

The changes in the molecular weight and MWD with different reaction temperatures are shown in Table III. M_n changed from 2.79×10^4 to 3.27×10^4. Its increase showed the same tendency of a high-molecular-weight component, and so did the polymerization degree. On the other hand, the MWD curve had better symmetry, and this meant the production was not mixtures of poly(methyl acrylate) and poly(butyl acrylate) homopolymers but almost MA/BA copolymers.[13]

However, when the temperature was too high, the sharp reaction made the system pressure increase rapidly and increased the reaction rate. Therefore, the suitable reaction temperature may have been 80°C.

Effect of the solvent on the copolymer properties

The different feeding methods could change the molecular weight and MWD of the copolymer and, moreover, the adhesive properties, when the same amount of the solvent was used. Table IV and Figure 5 show the details. The main reasons for the changes may be as follows. The autoacceleration reaction could only

TABLE II
M_n and MWD of Copolymers Prepared with Different Reaction Times

Sample	Time (h)		BA (1×10^{-3} mol/mL)		MA (1×10^{-3} mol/mL)		AIBN (1×10^{-5} mol/mL)		M_n	MWD
	Step 1	Step 2	Step 1	Step 2	Step 1	Step 2	Step 1	Step 2		
1	1	0	2.61		1.30		1.13		175,948	1.79
2	2	0.5	2.61	2.07	1.30	1.04	1.13	1.34	107,149	2.56
3	2	3	2.61	2.07	1.30	1.04	1.13	1.34	98,199	3.26

Reaction conditions: temperature = 80°C; atmosphere = nitrogen; feed method = batchwise; solvent = EA.

TABLE III
Molecular Weights and MWDs of Copolymers Prepared at Different Reaction Temperatures

Sample	Temperature (°C)	BA (1×10^{-3} mol/mL)		MA (1×10^{-3} mol/mL)		AIBN (1×10^{-5} mol/mL)		M_n	M_w	MP	MWD
		Step 1	Step 2	Step 1	Step 2	Step 1	Step 2				
1	70–75	2.61	2.07	1.30	1.04	1.13	1.34	27,921	74,204	86,868	2.66
2	75–80	2.61	2.07	1.30	1.04	1.13	1.34	30,835	74,847	93,657	2.43
3	80–85	2.61	2.07	1.30	1.04	1.13	1.34	32,776	75,084	92,647	2.29

Reaction conditions: atmosphere = nitrogen; feed method = batchwise; solvent = toluene.
[a] Weight-average molecular weight.

TABLE IV
Monomer and Initiator Densities with Different Amounts of the Solvents

Sample	BA (1×10^{-3} mol/mL)		MA (1×10^{-3} mol/mL)		AIBN (1×10^{-5} mol/mL)	
	Step 1	Step 2	Step 1	Step 2	Step 1	Step 2
1	2.61	2.07	1.30	1.04	1.13	1.34
2	2.20	2.07	1.10	1.04	9.54	1.34
3	1.80	2.07	8.97	1.04	7.79	1.34

Reaction conditions: temperature = 80°C; atmosphere = nitrogen; feed method = batchwise; solvent = EA. The monomer ratios were the same.

happen when the monomer density reached the critical value. Adding more solvent during the early stage of the polymerization could delay the appearance of the autoacceleration reaction and make the short-chain copolymer have larger molecular and lower molecular distributions. Therefore, the uniform chain length weakened the self-lubrication between the chains caused by the short chain and improved the stability of the substrate. However, because of the chain-transfer reaction with the solvent, the excess solvent amount (≧60 wt %) reduced the copolymer molecular weight and increased the molecular distribution, and so the adhesive properties became weaker. The change from 7.15 to 4.56 Pa s for the system viscosity and the lower high-shear resistance
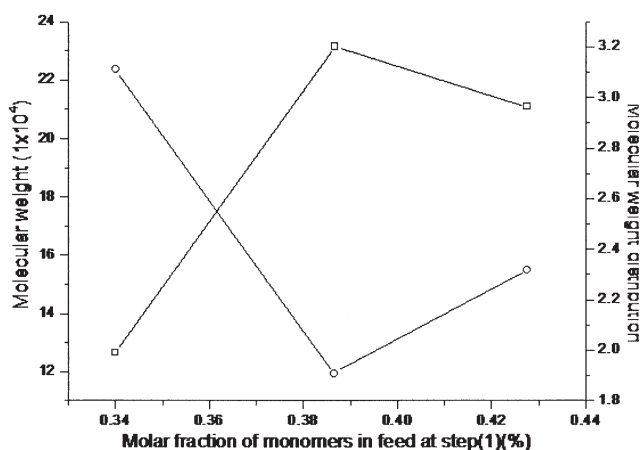
were also expressions of the lower molecular weight. Figure 6 shows the details.

Monomer reactivity ratios

Four MA and BA copolymer samples were prepared with different monomer ratios, as shown in Table V. The reactivity ratios were investigated with the extended Kelen–Tudos method.[7] It can be used to calculate reactivity ratios even when the rate of the mono-

Figure 5 Molecular weights and MWDs of copolymers with different monomers.
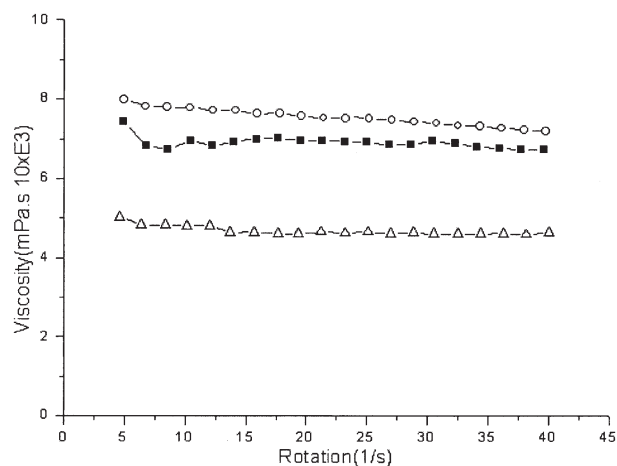

Figure 6 Relationship between the rotational speed and system viscosity: (○) viscosity of sample 1 (molar fraction of the monomers in the feed = 0.43), (■) viscosity of sample 2 (molar fraction of the monomers in the feed = 0.39), and (△) viscosity of sample 3 (molar fraction of the monomers in the feed = 0.34).

TABLE V
Different Monomer Ratios of Four Samples

Sample	MA mol	MA mL	BA mol	BA mL	AIBN 1×10^{-1} mol	AIBN g
1	0.166	15.04	0.047	6.69	7.74	0.1269
2	0.130	11.78	0.070	9.97	7.68	0.1260
3	0.088	7.98	0.110	15.67	8.26	0.1355
4	0.060	5.44	0.140	19.94	8.81	0.1445

Reaction conditions: temperature = 78°C; reaction time = 30 min; solvent (EA) volume = 30.2 mL.

$$\eta = (\gamma_1 + \gamma_2/\alpha)\xi - \gamma_2/\alpha$$

$$\zeta_1 = \zeta_2(Y/X), \qquad \zeta_2 = W(\mu+X)/(\mu+Y),$$

$$Z = \lg(1-\zeta_1)/\lg(1-\zeta_2)$$

$$F = Y/Z^2, \qquad G = (Y-1)/Z, \qquad \alpha = (F_{max} \cdot F_{min})^{\frac{1}{2}}$$

$$\eta = G/(\alpha+F), \qquad \xi = F/(\alpha+F)$$

Scheme 3 Kelen–Tudos method equations.

mer conversion is about 60%[14] because of its low deviation. The equations are shown in Scheme 3.

With η and ξ used to draw a rectilinear figure, a figure can give the reactivity ratio from the intercept and the slope coefficient. X is the molar ratio of MA to BA, whereas Y is the component ratio of the chain elements of MA and BA in the copolymer, which can be obtained from ^{1}H-NMR spectra. W is the conversion, and μ is the molecular weight ratio of MA to BA. γ_1 is the reactivity ratio of MA, whereas γ_2 is the reactivity ratio of BA. The ^{1}H-NMR spectra of the copolymer, shown in Figure 7, were used to analyze the copolymer compositions. The calculation data are summarized in Table VI.

The signal at 3.65 ppm (a) corresponds to —OCH$_3$ of MA, whereas the signal at 4.06 ppm (b) corresponds to —OCH$_2$— of BA in different copolymers synthesized with different monomer molar ratios, as shown in Table V.
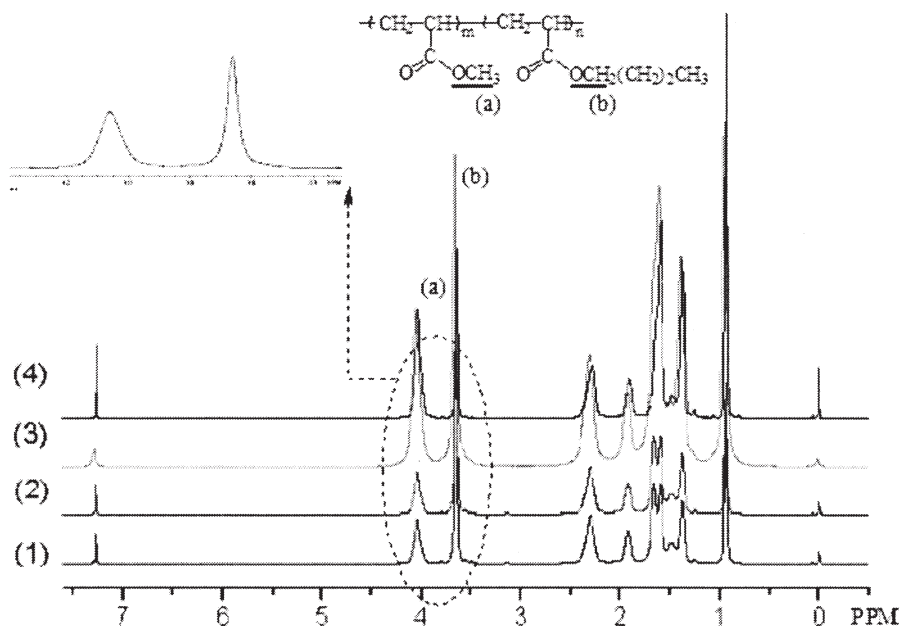
$$\mu = 1.489, \alpha = 1.503,$$

Figure 7 ^{1}H-NMR spectra of the copolymers: (1) sample 1, (2) sample 2, (3) sample 3, and (4) sample 4 (see Table I). ^{1}H-NMR (CDCl$_3$, δ): 0.93–0.97 [br, 3H, —COOCH$_2$(CH$_2$)$_2$CH$_3$], 1.26–1.80 (br, meso and racemo 2H, —CHCH$_2$—), 1.83–2.02 (br, meso 2H, —CHCH$_2$—), 2.31 (br, 1H, —CHCH$_2$—), 3.66 (s, 3H, —COOCH$_3$), 4.06 [m, 2H, —COOCH$_2$(CH$_2$)$_2$CH$_3$].

TABLE VI
Data for the Copolymerization of MA and BA Including the Extended Kelen–Tudos Parameters

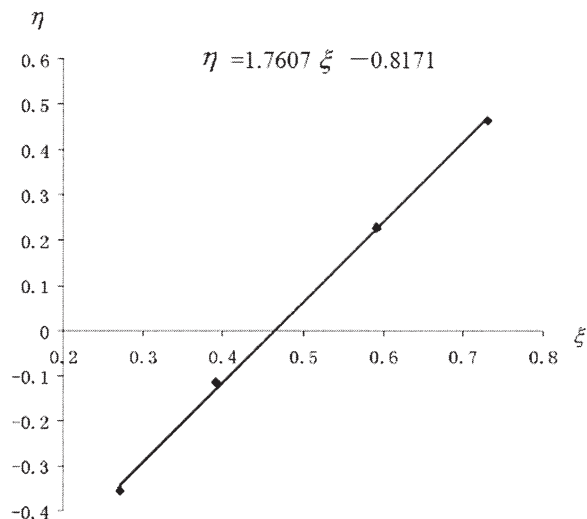| Sample	X	Y	W	Z	F	G	η	ξ
1	3.530	3.35	0.68	0.906	4.08	2.59	0.464	0.731
2	1.863	1.75	0.65	0.895	2.18	0.838	0.228	0.592
3	0.800	0.75	0.70	0.884	0.960	−0.283	−0.115	0.390
4	0.429	0.39	0.69	0.839	0.554	−0.727	−0.354	0.270

$\mu = 1.489$; $\alpha = 1.503$.

Figure 8 Rectilinear figure used to calculate the reactivity ratio.

As shown in Figure 8, the reactivity ratios of the two monomers were calculated as follows: 0.94 for MA and 1.23 for BA.

Effect of the molar fraction of the monomer in the feed on the copolymer properties

The copolymers prepared with different feed monomer molar ratios and calculated fractions of MA based on the reactivity ratios of the monomers are listed in Table VII. The adhesive properties of the copolymer prepared with different monomer molar ratios were investigated. Between the 16.7/83.3 and 50/50 BA/MA molar ratio compositions, the peel strength and hold character were effective, with a clear evolution from a rather elastic behavior to a rather viscoelastic behavior. The fibrillation phenomena[15] occurred during the release step, involving high film deformation and energy dissipation. The adhesive properties weakened between 50/50 and 83.3/16.7 because of the lowering of the cohesion force.

Figure 9 shows the changes in the adhesive properties of the copolymers with the peel strength and hold
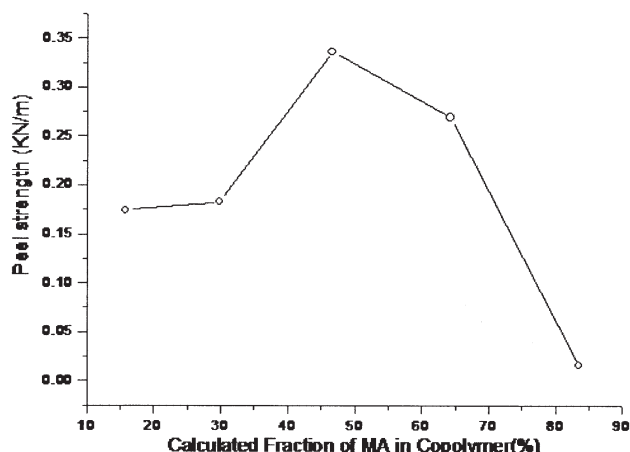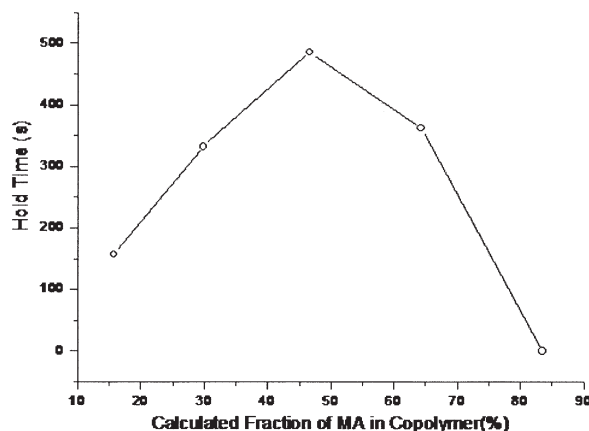
Figure 9 (a) Relationship between the MA molar ratio and copolymer peel strength and (b) relationship between the MA molar ratio and copolymer hold character (for the polymerize conditions, see Table VII).

time. Generalizing these two facts, we calculated that the best molar ratio of MA in the feed was 0.5 and hence 0.466 in the copolymer for PSAs. Here the ^{1}H-NMR spectra of copolymer C were used to analyze the copolymer compositions. The molar ratio of MA in the copolymer of 0.472, which was obtained by the inte-

TABLE VII
Different Component Ratios, Reaction Conditions, and Calculated Fractions of MA of the Resultant Copolymers

Sample	BA (1×10^{-3} mol/mL)		MA (1×10^{-3} mol/mL)		AIBN (1×10^{-5} mol/mL)		Solvent (mL)		Calculated fraction of MA in the copolymer
	Step 1	Step 2	Step 1	Step 2	Step 1	Step 2	Step 1	Step 2	
A	0.87	0.70	4.34	3.48	0.835	1.48	19.2	9.7	0.835
B	1.54	1.24	3.08	2.48	0.642	1.42	20.0	9.6	0.642
C	2.10	1.68	2.10	1.68	0.466	1.38	20.0	9.9	0.466
D	2.61	2.07	1.30	1.04	0.298	1.34	20.0	10.2	0.298
E	3.10	2.48	0.62	0.50	0.157	1.37	19.8	9.9	0.157

Reaction conditions: temperature = 78°C; solvent = EA; reaction time for step 1 = 2 h; reaction time for step 2 = 5 h.

gration of two character peaks, was very close to the theoretical value. In other words, with the feed method, the feed speed of the monomers could match the reaction velocity very well.

CONCLUSIONS

Batchwise feeding the initiator increased the copolymer molecular weight by 9%, reduced the MWD by 5%, and improved the adhesive properties obviously by increasing the overall conversions, but it did not influence the branch degree of the copolymer.

The suitable conditions were 7 h for the reaction time and 80°C for the reaction temperature for a homogeneous molecular structure.

The different solvent amounts affected the occurrence of the autoacceleration reaction and, moreover, the monomer conversions through the system viscosity. The suitable monomer mass ratio may have been 45 wt %.

We investigated the relationship between the adhesive characteristics and the fraction of MA in the copolymer. Using the Kelen–Tudos method to calculate the reactivity ratios of MA (0.944) and BA (1.228), we found that the MA fraction of 0.466 in the copolymer produced the best adhesive properties.

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