Synthesis of Monodisperse Poly(butyl acrylate) Initiated by SmMe(C$_5$Me$_5$)$_2$(THF) and Its Adhesive Properties After Crosslinking by Electron-Beam Irradiation

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ABSTRACT: Polymerization reactions of butyl acrylate (BuA) were carried out using an organosamarium complex, SmMe(C$_5$Me$_5$)$_2$(THF), as an initiator. Polymerization proceeds quantitatively to give high number-average molecular mass polymers (M_n > 200,000) and narrow molecular weight distributions (M_w/M_n < 1.07). Irradiation of the resulting poly(BuA) with an electron beam (EB) gave crosslinked poly(BuA). Improved viscoelastic and adhesive properties of these polymers were useful for high-temperature applications. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 432–437, 2001

Key words: poly(butyl acrylate); adhesive property; electron-beam irradiation; SmMe(C$_5$Me$_5$)$_2$(THF)

INTRODUCTION

A variety of acrylic polymers has been used as coating materials and pressure-sensitive adhesives, possibly because of their excellent heat and UV-light resistivity as well as their good adhesive properties against various substrates. Conventionally, such materials have been prepared using radical initiators, resulting in broad molecular mass distributions of >2.5 due to frequent chain transfers. This leads to an unfavorable effect on the mechanical properties of polymers, because low molecular mass components usually undergo deformation, resulting in a significant decrease of the cohesive strength of the materials.[1] Crosslinking is often used for adhesive polymers to improve their heat stability. The resulting polymers obtained by a radical initiator have low adhesive properties due to the gel formation for high molecular mass polymers, while the sol part exhibits only a low molecular mass fraction. Much attention has been paid to the synthesis of mono-disperse homopoly[alkyl (meth)acrylate]s by anionic polymerization.[2–7] These polymers show a relatively low number-average molecular mass (M_n < 100,000) and rather broad molecular mass distributions due to the preferred nucleophilic attack by an acidic α-H atom.[8–10] More recently, organo-rare earth metal complexes like SmMe(C$_5$Me$_5$)$_2$(THF)(C$_5$Me$_5$ = Cp*)[11] and YMeCp$_2^*$(THF)[12] have been reported as efficient initiators for living polymerization of alkyl methacrylates[13–15] and alkyl acrylates.[16,17] This article describes the crosslinking and pressure-sensitive adhesive properties of monodisperse poly(butyl acrylate) [poly(BA)] by electron-beam (EB) irradiation. The physical properties of these polymers were compared with those polymers obtained by conventional radical initiators.

EXPERIMENTAL

General

All experiments were carried out with standard Schlenk techniques under an argon atmosphere. Tetrahydrofuran, toluene, and hexane were pre-

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viously dried over CaH_2 for 4 days and distilled from a Na/K alloy before use. The solvents were thoroughly degassed by trap-to-trap distillation. Commercially available BA was dried over CaH_2 for 3 days, then over activated molecular sieves 4Å for 4 days, and distilled before use.

Preparation of 1,2,3,4,5-Pentamethylcyclopentadiene

Granular magnesium (7.5 g, 308 mmol) was placed in a 500-mL round-bottomed flask equipped with a reflux condenser and a 100-mL dropping funnel. Dry ether was placed in the flask and methyl iodide (17 mL, 273 mmol) dissolved in 70 mL of ether was slowly added to the magnesium from a dropping funnel. After stirring the mixture for 3 h at ambient temperature, a dry ether solution of 2,3,4,5-tetramethyl-2-cyclopentenone (33 mL, 219 mmol) was added dropwise up to 2 h at 0°C. After stirring the mixture overnight at ambient temperature, the reaction mixture was quenched with concentrated HCl (32 mL) dissolved in water (150 mL). After extracting the product with hexane (400 mL), the hexane solution was washed with an aqueous solution (200 mL) of Na_2CO_3 (30 g) and dried over Na_2SO_4. The desired product was obtained by distillation under reduced pressure (5 mm Hg/48–51°C); yield: 39.6% (12 g, 87 mmol).

Preparation of SmMe(C₅Me₅)₂(THF)

1,2,3,4,5-Pentamethylcyclopentadiene (10 mL, 64 mmol) was addded to a 75-mL THF dispersion of KH (2.4 g, 58 mmol) and the mixture was refluxed for 5 h to give a dispersion of KC_5Me_5 (9.6 g, 55 mmol). To a mixture of ICH_2CH_2I (6.8 g, 24 mmol) and 1.2 equiv of Sm granules (4.8 g, 29 mmol), 165 mL of THF was added and stirring was continued for 3 h at ambient temperature to produce $SmI_2(THF)_2$ as a blue–green solid (8.7 g, 16 mmol). The addition of KC_5Me_5 (50 mmol) to the THF solution (150 mL) of $SmI_2(THF)_2$ (24 mol) at 0°C resulted in a purple color and the precipitation of KI occurred. After stirring the mixture overnight, the product was centrifuged to remove the salt. The THF solution was concentrated and the recrystallization was carried out using a THF/hexane mixture to give $SmCp_2^*(THF)_2$ with a yield of 57.6% (7.9 g, 14 mmol). To a stirred toluene solution (100 mL) of $SmCp_2^*(THF)_2$ (3.4 g, 6 mmol), 5 equiv of $AlMe_3$ (3 mL, 31 mmol) was slowly added. While stirring for 24 h, a dark brown precipitate emerged in an orange solution.

Then, the mixture was extracted with hexane to separate $SmCp_2^*Me_2AlMe_2$ (insoluble) from the $AlMe_3(THF)$ and $AlMe_3$ part (soluble). The crude solid of $SmCp_2^*Me_2AlMe_2$ was then dissolved in 150 mL of toluene followed by cooling to −25°C to give red crystals of $SmCp_2^*Me_2AlMe_2$ (1.7 g, 3 mmol). Treating $SmCp_2^*Me_2AlMe_2$ with THF/hexane (1/3, 10 mL) followed by evaporation, dissolution into hexane (10 mL), and recrystallization at −25°C afforded $SmMeCp_2^*(THF)$ (1 g, 2 mmol) as orange crystals with a yield of 34%.

Polymerization of BA Initiated by SmMe(C₅Me₅)₂(THF)

To a toluene solution (40 mL) of BA (10 mL, 70 mmol), a toluene solution (1 mL) of $SmMeCp_2^*$-(THF) (8.2 mg, 0.016 mmol) was added at −78°C with vigorous stirring. The reaction was carried out at −78°C for 1–2 h and then the toluene solution was quenched with an excess of methanol. The resulting polymer was dried *in vacuo*. Typical yield: 97.5% (8.7 g).

Polymerization of BA Initiated by 2,2′-azobisisobutyronitrile (AIBN)

A 1-L round-bottomed flask was filled with an argon atmosphere and a mixture of BA (200 mL, 1.7 mol), ethanethiol (10 mL, 0.19 mol), and ethyl acetate (140 mL) was added to this flask. After the addition of AIBN (0.2 g, 1.2 mmol) at room temperature, polymerization proceeded at 60°C for 4 h and then at 70°C for 2 h. The reaction mixture was quenched by excess methanol. The resulting polymer was dried *in vacuo* with a yield of 99.9% (234 g).

Polymer Characterizations

^{1}H-NMR spectra were recorded on a JEOL-JNM-LA 400 spectrometer (400.13 MHz). Chemical shifts were calibrated using $CHCl_3$ (δ = 7.26 ppm). The number-average molecular mass M_n and molecular mass distributions were determined by gel permeation chromatography on a Tosoh SC-8010 high-speed liquid chromatograph equipped with a differential refractometer detector, in $CHCl_3$ as an eluent at 40°C. The columns used were TSK gel 4000_H, 3000_H, 2000_H, and 1000_H. The flow rate was maintained at 1.0 mL/min. The molecular mass was calibrated using the universal curve plotted with standard polystyrenes, whose M_n values were determined by the light-scattering method. These data are M_n = 8.70 × 10^2 (M_w/M_n equals; 1.10), M_n equals;

Table I   Polymerizations of BA Initiated by SmMe(C₅Me₅)₂(THF) at −78°C

Run	Polymerization Time (h)	[M]/[I] (mol/mol)	Observed			Calculated $M_n/10^{-4}$	Conversion (%)
			$M_w/10^{-4}$	$M_n/10^{-4}$	M_w/M_n		
1	1	250	3.71	3.60	1.03	3.20	84.5
2	1	390	5.03	4.90	1.03	5.00	92.1
3	2	1240	17.0	15.1	1.05	15.9	96.3
4	2	1560	20.3	19.5	1.04	20.0	95.6
5	2	2145	25.3	23.8	1.06	27.5	84.0
6	2	2480	37.4	34.9	1.07	31.8	80.2
7	2	3900	18.3	52.7	1.12	50.0	79.6

Polymerization conditions: solvent, toluene; toluene/[M₀] = 15 vol/vol.

2.63×10^3 (M_w/M_n equals; 1.05), M_n equals; 3.79 $\times 10^4$ (M_w/M_n equals; 1.01), M_n equals; 1.90 $\times 10^5$ (M_w/M_n equals; 1.04), and M_n equals; 2.89 $\times 10^6$ (M_w/M_n equals; 1.06).

Preparation of Tape Samples

The polymer solution (10–30 wt % in toluene) was cast to form a 25-μm-thick adhesive layer on a 25-μm-thick polyester film treated with a corona discharge. The cast film was dried for 5 min in a convection oven at 120°C and was aged for 48 h at 50°C. The resulting film was used as the adhesive-tape sample specimen.

EB Irradiation of Tape Samples

The adhesive-tape samples were EB-irradiated on an electron curtain CB 175/15/189L. The acceleration voltage was 165 kV. The total volume of irradiation was determined by measuring the gel percentage of the polymers.

Physical Properties as Pressure-sensitive Adhesives

The peel adhesion test was carried out against a stainless-steel plate. The tape sample specimen was cut into 25-mm-wide samples and rolled on a stainless-steel panel with a 24-kg rubber roller twice in each direction. The assembly was aged for 20 min at 23°C and the tape was peeled to the 180° angle direction at 300 and 5 mm/min peel rates at 23°C and 65% relative humidity. The holding power was measured as described below. The 10-mm-wide tape sample sheet attached to a stainless-steel panel was hung vertically and aged for 20 min at 40 and 80°C. On the end of a tape sheet, a 500-g load was put to measure the holding power. Downward movement from the

original position or the loading time before fracturing was measured for 1 h.

RESULTS AND DISCUSSION

Synthesis of Monodisperse Poly(BA)

In general, the degree of polymerization must exceed about 300 to show the physical properties as adhesives at a useful level. Therefore, we explored the synthesis of polymers with the molecular mass, $M_w > 30,000$, for pressure-sensitive adhesives. The results of the polymerizations are given in Table I. The SmMe(C₅Me₅)₂(THF)-initiated polymerizations of BuA followed a living polymerization route, giving high molecular mass polymers ($M_n > 100,000$) with narrow distributions ($M_w/M_n < 1.07$) in high conversions. The molecular mass of the resulting polymers was controlled by adjusting the monomer/initiator ratio. All the polymerizations quantitatively proceeded within a short time. In the case of polymers with $M_n > 500,000$, the polydispersity was higher because the growing end was sensitive to moisture and oxygen contaminated in the mono-

Table II   Polymerization of BA Initiated by AIBN

Run	Observed			Conversion (%)
	$M_w/10^{-4}$	$M_n/10^{-4}$	M_w/M_n	
8	9.2	5.0	1.83	100
9	27.0	8.2	3.31	99
10	101.3	29.1	3.47	99

Polymerization conditions: temperature, 70°C; polymerization time, 4 h; solvent, toluene.

Table III   Molecular Weights and Crosslinking of Polymers Before and After EB Irradiation

Run	Initiator	Before EB Irradiation[a]			Volume of EB[b] (kg)	Degree of Crosslinking[c] (%)	After EB Irradiation (Sol Part)[a]		
		$M_w/10^4$	$M_n/10^{-4}$	M_w/M_n			$M_w/10^{-4}$	$M_n/10^{-4}$	M_w/M_n
6	SmMe(C$_5$Me$_5$)$_2$ (THF)	37.4	34.9	1.07	60	51.3	57.2	30.9	1.85
6′	SmMe(C$_5$Me$_5$)$_2$ (THF)	37.4	34.9	1.07	90	71.4	44.3	22.8	1.94
9	AIBN	32.6	8.20	3.98	90	45.6	32.4	7.4	4.38
9′	AIBN	32.6	8.20	3.98	150	64.2	15.7	5.2	3.02
7	SmMe(C$_5$Me$_5$)$_2$ (THF)	118.2	105.5	1.16	30	63.3	89.4	27.3	3.27
10	AIBN	105.6	29.0	3.64	30	60.5	70.1	19.7	3.56

[a] Determined by GPC.
[b] Accelerating voltage 165 kV.
[c] Determined by measuring the insoluble part in toluene.

mer and the solvent. The stereoregularity obtained by SmMeCp$_2^*$(THF) was very poor and this system gave only an atactic polymer ($mm = 24$, $mr = 51$, $rr = 25\%$) as evidenced by NMR. Radical polymerization of BuA using an AIBN initiator was also carried out to study its adhesive property in comparison with the poly(BuA) bearing very low polydispersity (Table II).

Crosslinking Reactions

Crosslinking of poly(BuA) by the EB resulted in the formation of a gel. The total amount of the gel in the polymers was adjusted by changing arbitrarily the volume of EB irradiation. Thus, we could prepare polymers with nearly the same gel value from both the polymer initiated by a rare earth metal complex and that obtained by a radical initiator. Table III shows the molecular mass of the sol fraction before and after EB irradiation. Here, we used nearly the

same M_w for both polymers before EB irradiation (runs 6 and 9, runs 7 and 10). Poly(BuA) obtained by SmMeCp$_2^*$(THF) kept its narrow molecular weight distribution even when the polymer was EB-irradiated.

Pressure-sensitive Adhesive Properties

The pressure-sensitive adhesive properties of poly(BuA) after crosslinking were measured. The resulting holding powers and the peel strengths are summarized in Table IV. The measurement of the holding powers indicates no creep at 80°C after more than 2 h for both high and low molecular mass monodisperse polymers obtained by SmMeCp$_2^*$(THF), while the polymers obtained by radical polymerization show the holding time at less than 40 min at 80°C due to the presence of a low molecular mass component. At 40°C, no difference between the polymers obtained by

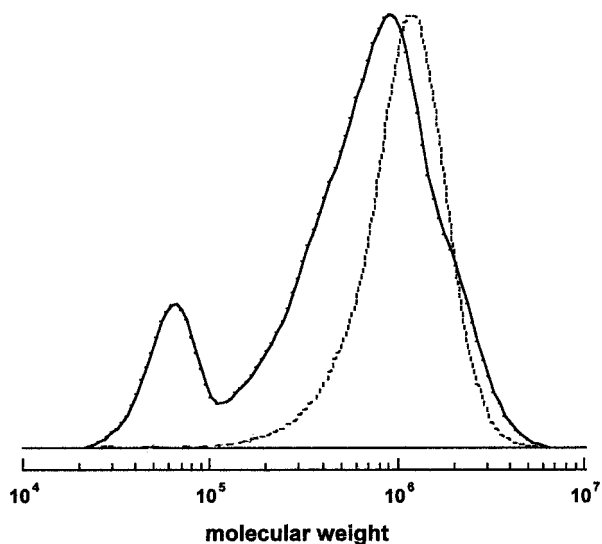**Table IV   Adhesive Properties of Poly(BA) After EB Irradiation**

Run	Initiator	Holding Time (min)[a]		180° Peel Strength (gf/20 mm)[b]	
		80°C	40°C	300 mm/min	5 mm/min
6	SmMe(C$_5$Me$_5$)$_2$(THF)	>120	>120	440	453(cf)[c]
6′	SmMe(C$_5$Me$_5$)$_2$(THF)	>120	>120	334	265
9	AIBN	40	>120	527	152(cf)[c]
9′	AIBN	5	0	412	82
7	SmMe(C$_5$Me$_5$)$_2$(THF)	>120	>120	333	302
10	AIBN	25	>120	540	235

[a] Downward movement of the polymer layer or the time before fracturing.
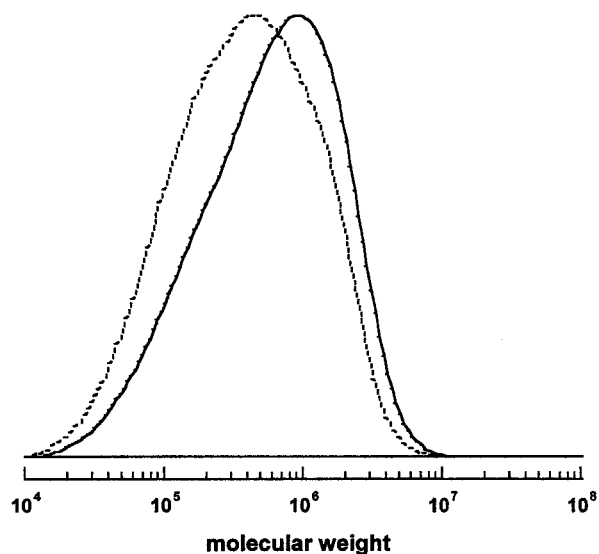[b] Measured against SUS.
[c] Cf: cohesive failure.
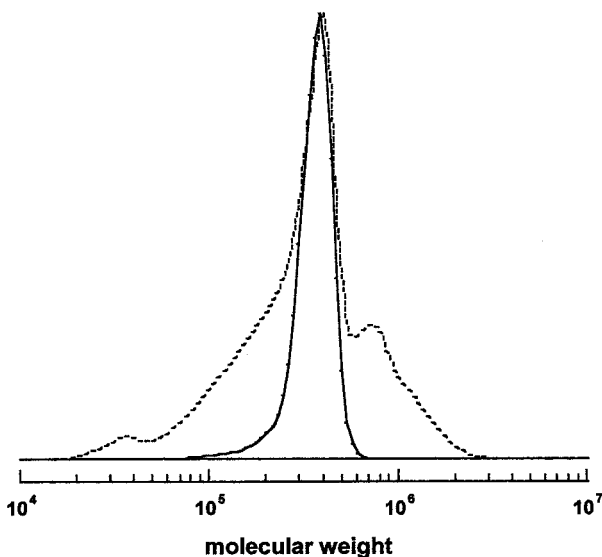
Figure 1 Gel permeation chromatographs of low molecular weight poly(BuA) initiated by SmMe(C$_5$Me$_5$)$_2$(THF) (run 6) (——) before and (----) after EB irradiation.

Figure 3 Gel permeation chromatographs of poly-(BuA) initiated by AIBN (run 10) (——) before and (----) after EB irradiation.

SmMeCp$_2^*$(THF) and AIBN was observed. Also, we could not find any advantage of the polymer obtained by SmMeCp$_2^*$(THF) in the measurement of the peel strength at the rate of 300 mm/min. However, polymers obtained using SmMeCp$_2^*$(THF) showed very little peel rate dependency, while the polymers obtained by AIBN vary their holding power by changing the peel rate due to the presence of a low molecular mass component. Thus, we could find excellent peel strength using the
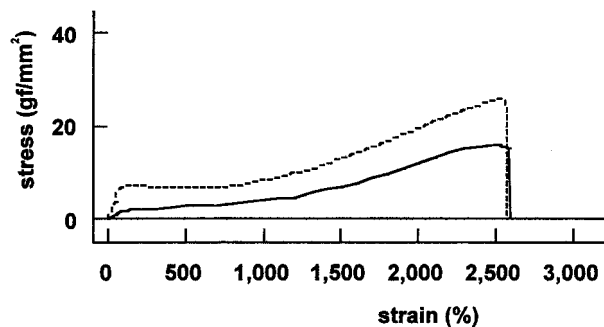
monodisperse polymer even for the peel strength at 5 mm/min for both low and high molecular polymers.

To reveal the reason why the monodisperse polymer shows excellent peel strength, we measured the GPC profiles before and after EB irradiation. Figure 1 indicates the formation of both high and low molecular polymers from the relatively low molecular mass monodisperse poly-(BuA) after by EB irradiation. Thus, a unimodal polymer changes to a tri-modal polymer. High molecular mass polymers may be obtained by radical coupling of the cleaved polymer fraction and the low molecular mass polymers are formed by radical scission of a monodisperse polymer. In contrast to these behaviors of relatively low molecular polymers, high molecular mass monodis-

Figure 2 Gel permeation chromatographs of low molecular weight poly(BuA) initiated by SmMe(C$_5$Me$_5$)$_2$(THF) (run 7) (----) before and (——) after EB irradiation.

Figure 4 Stress–strain curves of low molecular weight poly(BuA) obtained by (----) SmMe(C$_5$Me$_5$)$_2$(THF) (run 6) and (——) AIBN (run 9) after EB irradiation.
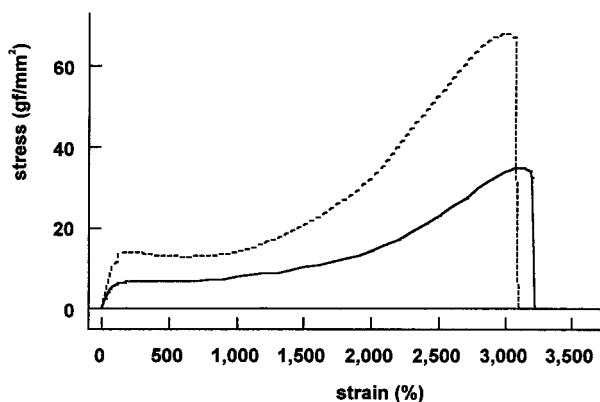
Figure 5 Stress–strain curves of high molecular weight poly(BuA) obtained by (- - - -) $SmMe(C_5Me_5)_2$ (THF) (run 7) and (——) AIBN (run 10) after EB irradiation.

perse polymers preferentially produce the low molecular polymer fraction after EB irradiation, without production of a much higher molecular mass polymer fraction (Fig. 2). Thus, the resulting polymers exhibit a low molecular mass polymer fraction and, hence, increased tackiness. The high molecular mass poly(BuA) obtained by AIBN shows a broad GPC profile before EB irradiation, but only a small change after the EB irradiation (Fig. 3). Actually, the formation of a relatively low molecular weight polymer was observed, but the whole pattern was not greatly changed. Therefore, the holding time at 80°C and the peel strength at the rate of 5 mm/min are lower for the polymer obtained by AIBN than those for the monodisperse polymers. Figure 4 shows the stress–strain curve for the low molecular mass poly(BuA), and Figure 5, that for the high molecular mass poly(BuA). Relatively high stress was observed at low strain for poly(BuA) obtained by $SmMeCp_2^*$(THF) due to the lack of a low molecular weight fraction as shown in Figure 4. Moreover, for high molecular mass poly(BuA), high stress was observed, especially for the polymer obtained by $SmMeCp_2^*$(THF) at a strain value of 3000%. Thus, excellent adhesive performance was observed for the first time for the poly(BuA) after EB irradiation.

CONCLUSIONS

The synthesis of high molecular mass poly(BA) ($M_n > 35 \times 10^4$) with narrow distributions ($M_w/M_n < 1.07$) was achieved using $SmMe(C_5Me_5)_2$(THF) as an initiator. The cast films of these polymers exhibit good adhesive properties when compared to the polymers obtained by radical initiators. In particular, holding tests showed that the polymers obtained by $SmMeCp_2^*$(THF) are maintained for more than 120 min even at 80°C. In addition, the stress–strain tests reveal high-stress and the high-strain characters for the polymers obtained by $SmMeCp_2^*$(THF) after EB irradiation. Monodisperse polymers are effective for use as adhesive materials.

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