

# Synthesis and Characterization of Lacquers Based on Styrene Acrylic Copolymers for Applications in Leather Industry

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## Synopsis

Radical copolymerization of styrene with butylacrylate and/or maleic anhydride was carried out at 70°C, using benzoyl peroxide as an initiator in benzene/ethylacetate in order to prepare lacquers for top coats for use in leather industry. Copoly(styrene-butylacrylate) was characterized using IR and <sup>13</sup>C-NMR spectroscopy. Thermal properties of the polymers were studied using thermogravimetric analysis and evaluated the integral procedural decomposition temperatures of polymers. The order of reaction and the activation energy for the thermal degradation of polystyrene, poly(ST-co-MAN) and St-BA-MAN terpolymer at different temperatures were calculated. Molecular weights were determined from gel permeation chromatography and viscosity measurements. Physical properties of the films were studied and compared with standard lacquers available for top coats in leather industry.

## INTRODUCTION

Nitrocellulose (NC)-based polymeric lacquers are now employed extensively in the leather industry because of their relative ease of application as top coat to impart essential properties such as flexural endurance, scuff resistance, dry and wet rub resistance, abrasion resistance, air, and water vapor permeability to the leather. However, NC-based lacquers have certain disadvantages such as fire hazard and inherent explosive character. NC films have also a tendency to take up color on aging or on exposure to light. Further, the film begins to crack on leather on aging due to migration of plasticizers used along with the formulations. In order to overcome these defects in NC lacquers, it was considered desirable to develop a finish in which the plasticizing effect was introduced by chemical combination with the film forming monomeric units in the polymer backbone. This was achieved partly to some extent by grafting different acrylic monomers to the backbone of the film forming chlorinated rubber.<sup>1-3</sup>

The present work was undertaken to synthesize a series of new lacquers based on co/terpolymers of butylacrylate, styrene and/or maleic anhydride and evaluate their ability to overcome the deficiencies observed in lacquers currently available to the leather industry.

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## EXPERIMENTAL

### Materials

Styrene (Aldrich) and butylacrylate (Aldrich) containing p-t-butylcatechol inhibitor was purified by extraction with 5% NaOH in water followed by drying with MgSO<sub>4</sub> and calcium hydride and vacuum distillation. Maleic anhydride (LR, Loba Chem) was recrystallized from chloroform to mp 63°C. Benzoyl peroxide (LR, Loba Chem), benzene, toluene, ethylacetate, and tetrahydrofuran were used as received.

### Polymerization

The calculated amounts of monomers were dissolved in solvent (benzene/ethylacetate) contained in a three-necked flask fitted with a thermometer, nitrogen inlet, condenser, and a mechanical stirrer. The flask was heated in a thermostatic water bath at  $70 \pm 0.1^\circ\text{C}$ . The polymerization was allowed to continue for 9–10 h after the addition of the initiator (2%). Copolymers synthesized from different feed ratios of styrene and butylacrylate (monomer/solvent: 1/2) are homogenous solutions in benzene and ethylacetate. These copolymers (62–89% conversion) were precipitated using petroleum ether. In the case of benzene as solvent, a white precipitate separated out for terpoly(styrene–butylacrylate–maleic anhydride), which was filtered and dried in vacuum at 20°C.

### Polymer Characterization

#### *IR Spectroscopy*

A Shimadzu-408 IR spectrophotometer was used. Thin films of the polymer samples were prepared from the ethylacetate solution of the polymers having concentration, 0.1 g/mL. The solutions were cast on a glass plate at room temperature. After solvent was slowly evaporated, the resultant films were dried under vacuum at 25°C for 24 h to remove trace amounts of solvent/monomer before characterization.

#### *<sup>13</sup>C-NMR Spectroscopy*

Fourier transform (FT) <sup>13</sup>C-NMR spectrum was recorded using a Bruker-CXP 22.64 MHz spectrophotometer. Homo and copolymer samples were examined as 15–20 (w/v) solutions in d<sub>6</sub>-benzene as solvent, using TMS as internal reference at 25°C.

#### *Thermogravimetric (TG) Analysis*

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) curves were recorded with a DuPont microthermobalance. An aliquot sample weighing 10 mg was used for TGA/DTG analysis at the rate of 20°C min temperature rise using nitrogen flow rate of 80 mL/min.

*Viscosity Measurements*

The viscosity measurements were made with an Ubbelohd type dilution viscometer and the solutions were thermostated at 25°C. Intrinsic viscosity was determined from plots by extrapolating inherent viscosity to zero concentration. Flow times were kept above 100 s to minimize kinetic energy corrections.

*Gel Permeation Chromatography*

The weight average molecular weight ( $\bar{M}_w$ ) and the number average molecular weight ( $\bar{M}_n$ ) were determined by the gel permeation chromatography. Approximately 0.2 mL of a 1% polymer in tetrahydrofuran solvent was used at a flow rate of 2 mL/min. The GPC was calibrated using narrow molecular weight polystyrene standards of known molecular weight. The molecular weights are not corrected for peak broadening and for the variation of refractive index with molecular weight.

*Measurement of Tensile Strength and % Elongation*

Using a die-test, specimens were cut as per the ASTM standard procedures. The specimens of even thickness were selected by measuring the thickness of the film using the thickness gauge having a sensitivity of the order of 0.0001. Films were mounted on a cardboard and conditioned again. Individual test films were removed from the desiccator and tested immediately using Instron universal testing machine.

**RESULTS AND DISCUSSION**

Nine copolymers of styrene (St) and butylacrylate (BA) were synthesized according to experimental details given in Table I using benzoyl peroxide (2% based on the weight of monomers) as the initiator. The copolymerizations

TABLE I  
Preparation and Film Properties of Styrene-Butylacrylate Copolymers<sup>a</sup>

Serial no.	Styrene (g mmol)	Butylacrylate (g mmol)	Yield (%)	Film property <sup>b</sup>	
				Physical property	Elongation (%)
1	2.60 (25)	9.60 (75)	89	Very tacky	365
2	4.16 (40)	7.68 (60)	85	Very tacky	241
3	4.68 (45)	7.04 (55)	82	Tacky	193
4	5.20 (50)	6.40 (50)	78	Slightly tacky	154
5 <sup>c</sup>	5.72 (55)	6.76 (45)	74	Nontacky	106
6	5.93 (57)	5.50 (43)	71	Slightly tacky	80
7	6.24 (60)	5.12 (40)	69	Brittle	—
8	6.56 (63)	4.47 (37)	65	Powdery	—
9	7.18 (69)	3.97 (31)	62	Powdery	—

<sup>a</sup>Temperature 70°C, solvent ethylacetate; benzoylperoxide, 2% (2% catalyst is taken on the basis of the weight of monomers); polymerization time 9–10 h.

<sup>b</sup>Films reported here were taken from the polymers obtained in ethylacetate medium.

<sup>c</sup>The glass transition temperature for this copolymer is found to be 1.92°C.

TABLE II  
Preparation of Terpolymers Based on Styrene, Butylacrylate, and Maleic Anhydride\*

Serial no.	Styrene	BA (g)	MAn (g)	Film property on		Bally's flexometer reading: No. of flexings at which		
				Glass plate	Leather	Film cracks	Grain cracks	Leather cracks
1	5.72	5.76	0.49	Brittle	Brittle	18,000	Withstands 75,000	Withstands 75,000
2	5.72	5.12	0.49	Brittle	Brittle	11,500	Withstands 75,000	Withstands 75,000
3	5.20	5.76	0.49	Flexible, nontacky	Flexible, nontacky	Withstands 75,000	Withstands 75,000	Withstands 75,000
4	5.51	5.38	0.49	Brittle	Brittle	13,600	Withstands 75,000	Withstands 75,000
5	5.20	5.12	0.98	Brittle	Brittle	6400	Withstands 75,000	Withstands 75,000
6	NC	lacquer	(Control)	Flexible, nontacky	Flexible, nontacky	Withstands 75,000	Withstands 75,000	Withstands 75,000

\* Film obtained in the case of experiment 5 is not transparent.

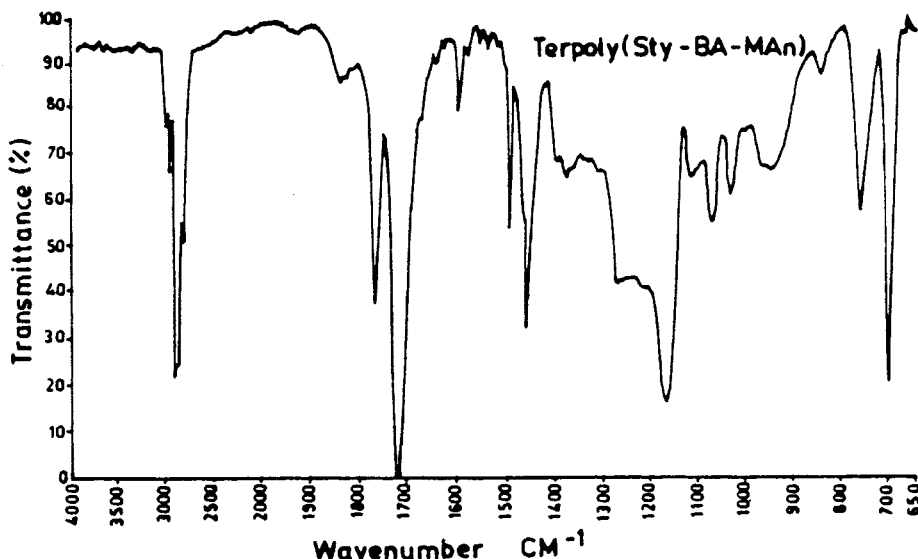


Fig. 1. IR spectrum (cast film) of styrene-butyl acrylate-maleic anhydride (50/45/5, mmol) terpolymer.

were homogenous in ethylacetate and benzene. The film properties of the copolymers such as % elongation and the physical property (tackiness) were also studied. Copolymer having the feed composition of 55 mmol of styrene and 45 mmol of butylacrylate gave a film without tackiness having a reasonable % of elongation (136) to employ for topcoat in leather finishing. By taking this feed composition as a standard composition, attempts were made to incorporate maleic anhydride ( $MA_n$ ) to give internal plasticizing effect and thereby to achieve more water repellancy and flexibility of the film. The results of the terpolymerization are given in Table II. Due to the reactivity ratios ( $r_{SA} = 0.6$  and  $R_{AS} = 0.28$ ), compositional drift is expected in these copolymers. However, in the present experimental conditions, the composition of the copolymers is reproducible within the experimental errors.

The IR spectra of the terpoly(ST-BA- $MA_n$ ) (Fig. 1) showed absorption bands typical of the constituent monomeric units their relative intensity depending on composition. Absorptions at  $1850$  and  $1735\text{ cm}^{-1}$  ( $\nu_{C=O}$  for maleic anhydride and ester carbonyl group),  $3055$  and  $1600\text{ cm}^{-1}$  ( $\nu_{C-H}$  and  $\nu_{C=C}$  of aromatic ring),  $2830$ - $2815\text{ cm}^{-1}$  ( $\nu_{C-H}$  of butyl group) were conspicuous.

Although the spectra of polystyrene<sup>4</sup> and polybutylacrylate<sup>5</sup> have been described in the literature, the copoly(ST-BA) spectrum is not reported. <sup>13</sup>C-NMR spectrum of the copoly(ST-BA) is presented in Figure 2. The chemical shift of each carbon atoms is confirmed from the off-resonance <sup>1</sup>H-decoupled spectra of the copolymer. Peaks due to carbon atoms attached to none, one or two hydrogen atoms appears as a singlet, doublet, or triplet respectively.

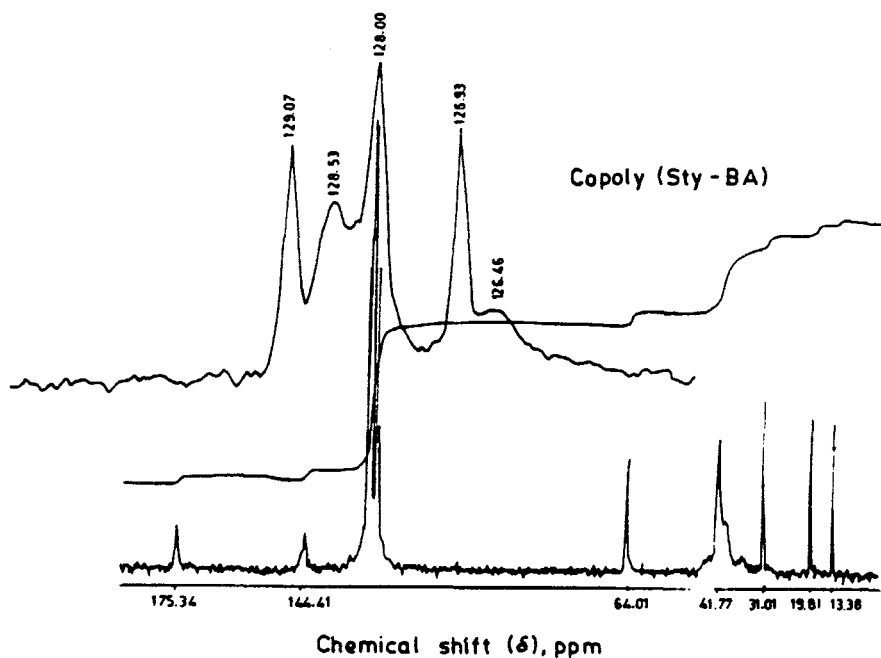


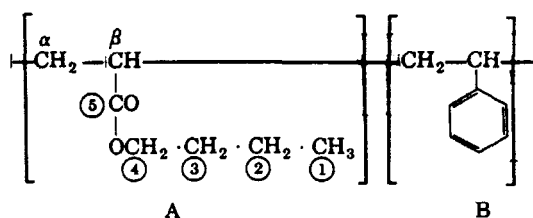
Fig. 2.  $^{13}\text{C}$ -NMR spectrum of styrene-butylacrylate (55/45, mmol) copolymer with  $\overline{M}_n$ , GPC = 8206; 22.64 MHz, 37,275 accumulations.

Chemical shift ( $\delta$ , ppm) assignments for the monomer unit A (Scheme 1) are given below:

$$\begin{aligned} \delta_{\text{CH}_3}(1) &= 13.88; & \delta_{\text{CH}_2}(2) &= 19.51; & \delta_{\text{CH}_2}(3) &= 31.01; \\ \delta_{\text{OCH}_2}(4) &= 64.01; & \delta_{\text{CO}}(5) &= 175.34; & \delta_{\text{CH}_2} &= 35.36; \\ \delta_{\text{CH}} &= 41.79 \text{ ppm} \end{aligned}$$

The assignment for the monomer unit B: aromatic ring:  $\delta = 144.41$ ; 129.07 and 128.53; 128.0, 126.95;  $\delta_{\text{CH}} = 40.38$ ;  $\delta_{\text{CH}_2}$ , not clear.

The integrated areas of peaks in the  $^{13}\text{C}$  spectra are believed to be a measure of the contributions of the various carbon types to the polymer structure. The ratio of the peak area at 144 ppm corresponds to the  $^{13}\text{C}$  in the styrene unit to that of the carbonyl group ( $^{13}\text{C}$ ) in the butylacrylate gives the quantitative % composition of the monomeric units in the copolymer.



Scheme 1

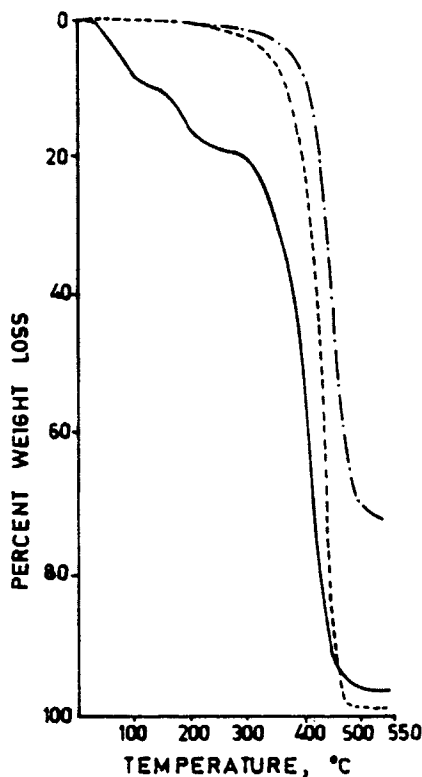


Fig. 3. TGA curves for polymers in nitrogen with a heating rate of  $10^{\circ}\text{C}/\text{min}$ : (a) (.....) polystyrene; (—) styrene-MAn (1/1) copolymer; (---) St-BA-MAn (50/45/5, mmol) terpolymer; (b, c, and d) graphs of the first derivative ( $-\Delta-\Delta-$ ) of the thermogravimetric curve ( $dw/dt$ ) and the weight of reactant ( $W_r$ ) ( $-\circ-\circ-$ ) plotted as a function of reciprocal absolute temperature for the degradation of polystyrene, poly(St-Co-MAn) and terpoly(St-BA-MAn), respectively.

Quantitative estimation of the % composition of St-BA copolymer was determined by  $^1\text{H-NMR}$  spectroscopy as follows: Let  $x$  be the mole fraction of styrene; then  $(1 - x)$  is that of butylacrylate. The total number of protons in each monomeric unit is in the ratio of 2 : 3.

$$\frac{x}{2} + \frac{(1 - x)}{3} = \frac{\text{area of downfield aromatic protons}}{\text{area of total protons}} = A$$

This on simplification gives  $x = 6A - 2$ . From the equation, the mole fraction of styrene ( $x$ ) was calculated from the area of downfield aromatic protons (6.37–7.38 ppm) to that of the total area of protons. This type of treatment was given earlier for determining the reactivity ratios of MA-MMA copolymer.<sup>6</sup>

TGA curves for the polystyrene, copoly(St-MA<sub>n</sub>), and terpoly(St-BA-MAn) are presented in Figure 3(a) and the results of the differential gravimetric analysis in Table III. Poly(St) was found to be stable to heating up to  $500^{\circ}\text{C}$  and maximum degradation (71%) occurs around  $500^{\circ}\text{C}$ . The fact that styrene with MAn forms alternate copolymers was well established in the literature. In the case of copoly(St-MAn), complete degradation of maleic

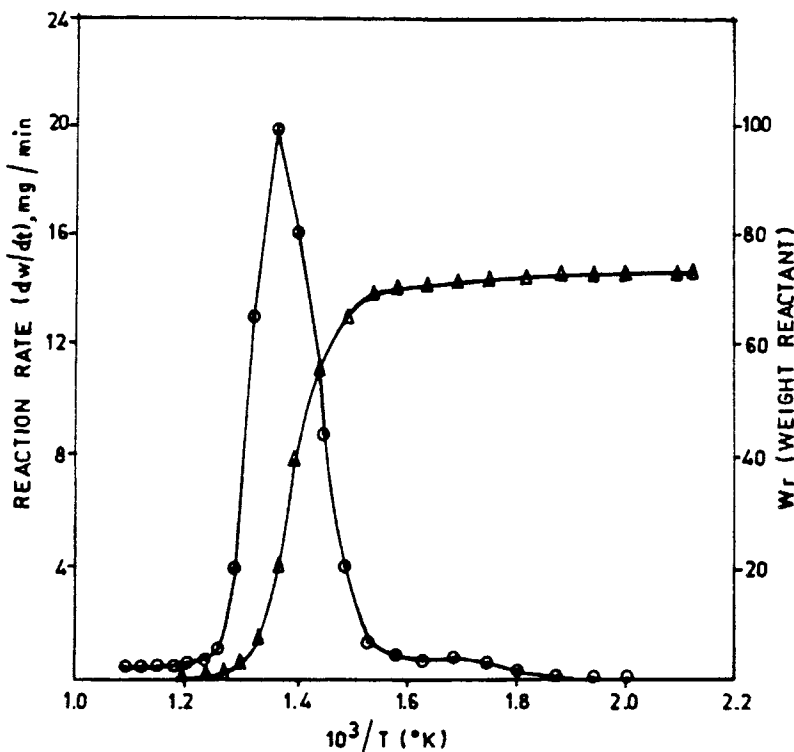


Fig. 3. (Continued from the previous page.)

anhydride took place around 200°C, whereas styrene degrades around 420°C. The presence of maleic anhydride in the polymeric chain may be responsible for bringing down the degradation temperature of styrene units from 500 to 420°C. Terpoly(St-BA-MAn) has three degradation peaks corresponding to styrene, butylacrylate, and maleic anhydride at 425, 460, and 195°C respectively. At 500°C, the weight loss for poly(St), copoly(St-MAn) and terpoly(St-BA-MAn) were found to be 71, 69, and 98%, respectively.

The kinetics of the thermal degradation of poly(St), poly(St-Co-MAn) and terpoly(St-BA-MAn) were studied from their TGA curves by employing the Freeman-Carroll equation<sup>7</sup>

$$\Delta \log(dw/dt) = x \log W_r - (\Delta E' / 2.3R) \Delta(1/T)$$

where  $dw/dt$  is the rate of the reaction,  $x$  is the order of the reaction,  $\Delta E'$  is the energy of activation;  $W_r = \Delta W_c - \Delta W$  (proportional to the amount of reactant),  $\Delta W$  being the weight loss at the point where  $dw/dt$  is taken and  $\Delta W_c$  being the total loss associated with given reaction.

A simple method to determine  $dw/dt$  and  $W_r$  at constant  $\Delta(1/T)$  is to plot the first derivatives of the primary thermogravimetric curve and the corresponding  $W_r$  (proportional to weights of reactants) as a function of reciprocal absolute temperatures. These graphs are shown in Figures 3(b), 3(c), and 3(d) for the thermal degradation of polystyrene, poly(St-Co-MAn), and terpoly(St-BA-MAn) under nitrogen atmosphere, respectively.



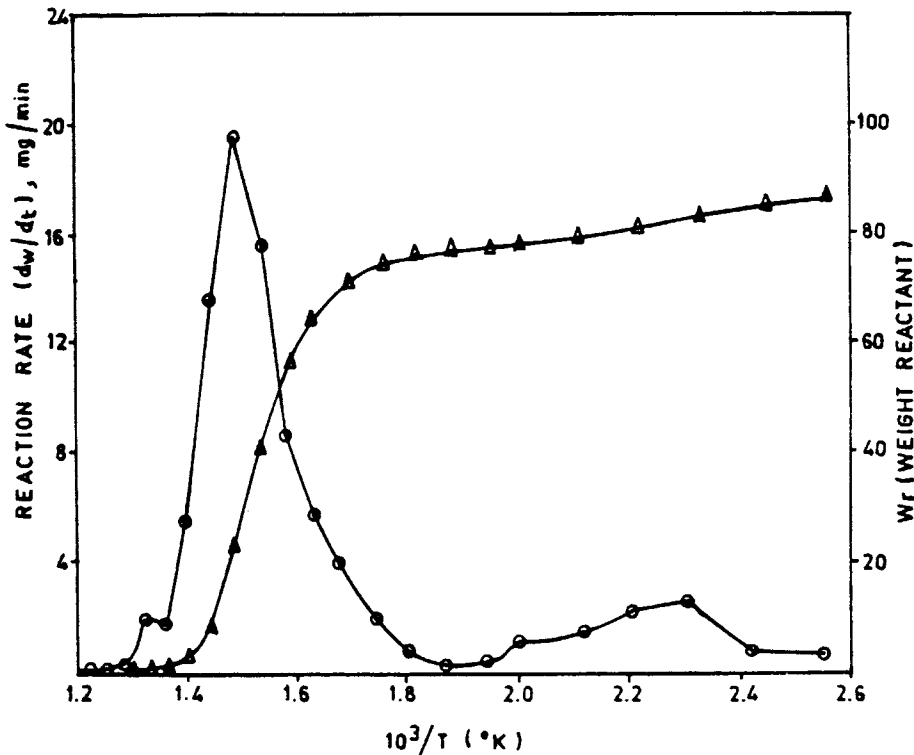


Fig. 3. (Continued from the previous page.)

The order of the reaction ( $x$ ) is determined from the intercept extrapolated to  $\delta \log W_r = 0$  and the energy of activation ( $\Delta E^*$ ) from the slope by plotting  $\Delta \log W_r$  [kept  $\Delta(1/T)$  constant] against  $\Delta \log(dw/dt)$ . The order of the thermal degradation reaction and the energy of activation at different temperature ranges are given in Table IV.

Molecular weights of the copolymers were determined by viscosity measurement and GPC. In the first case, intrinsic viscosity or limiting viscosity (LVN) of the polymer solutions were determined by two methods: graphical and the Solomon-Ciuta algebraic method using the flow rates of different concentrations of styrene-butylacrylate (55/45 mmol) copolymer solution. Graphical method [Fig. 4(a)] require an extrapolation to zero concentration to obtain the intrinsic viscosity. The Solomon-Ciuta method,  $[\eta] = 1/C \sqrt{2(n_{sp} - \ln \eta_r)}$ , gives the intrinsic viscosity from the viscosity ratio measured at a concentration such that  $\eta_{sp} = 0.6$ . These two methods yield comparable results  $[\eta]$  graphical = 0.143;  $[\eta]_{S-C} = 0.135$ . The Mark-Houwink-Sakurada equation was used with appropriate constants for styrene (atactic) in benzene ( $K \times 10^3$ ) = 100;  $\alpha = 0.5$ <sup>8</sup> to determine the weight average molecular weight of copolymer of styrene-butylacrylate (55/45, mmol) by viscometry ( $\bar{M}_{w,v} = 19,320$ ).

The number average molecular weight ( $\bar{M}_n$ ), the weight average molecular weight ( $\bar{M}_w$ ), and the polydispersity index of St-BA (55/45 mmol) copolymer using GPC [Fig. 4(b)] were found to be  $\bar{M}_n = 8206$ ,  $\bar{M}_w = 19,203$ , and  $\bar{M}_{w,v} =$

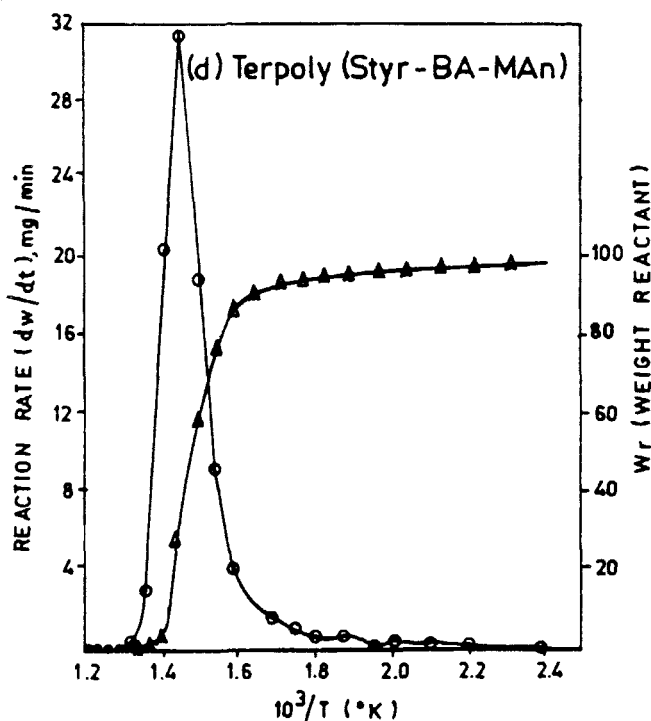


Fig. 3. (Continued from the previous page.)

TABLE III  
Differential Gravimetric Analysis Data of Polystyrene, Copoly(St-MAn)  
and Terpoly(St-BA-MAn)

Sample	Temperatures at different percent weight loss									
	(%)	10	20	30	40	50	60	70	80	90
Poly styrene		400	425	435	445	455	465	495	—	—
St-MAn (1:1) copolymer		125	300	355	380	395	410	415	425	445
St-BA-MAn (53:42:5 mmol) terpolymer		375	400	410	420	425	435	440	445	455

19,320) respectively. The weight average molecular weight determined both from GPC and viscosity measurements were found to be in good agreement. Bevington et al.<sup>9</sup> reported that in the homopolymerization of styrene, the polymeric radicals undergo termination, mainly by recombination. Butylacrylate radicals terminate predominantly by disproportionation as reported in the case of (meth)acrylates.<sup>10</sup> The theoretical values of  $\bar{M}_w/\bar{M}_n$  for polymer produced via radical recombination and radical disproportionation are 1.5 and 2.0, respectively.<sup>8</sup> The value of  $\bar{M}_w/\bar{M}_n$  in copolymerization is also known to depend on the chain termination mechanism in the same way as it does in the

TABLE IV  
Order of Reaction and the Activation Energy for the Thermal Degradation of Polystyrene,  
Poly(St-Co-MAn) and (St-BA-MAn) Terpolymer at Different Temperatures

Polymer	Temp (°C)	Order of reaction	$\Delta E'$ (kcal/mol)
Polystyrene	0-320	0	24.3
	350-400	0.6	57.1
	400-480	0.5	9.4
	480-560	1.0	29.3
Poly(St-Co- MAn)	140-160	0.2	36.6
	280-340	0.5	30.5
	340-450	0.5	21.1
(St-BA-MAn) terpolymer	Up to 340	0.3	17.4
	400-410	0.4	29.5
	410-430	0.6	10.2

respective homopolymerizations.<sup>11</sup> The value of  $\bar{M}_w/\bar{M}_n = 2.34$  clearly suggests that there is a tendency for disproportionation mechanism to terminate the polymeric chains.

Five films of even thickness were tested for tensile strength properties. The tensile strength and the % elongation were calculated as follows:

$$\text{Tensile strength} = \frac{\text{breaking load (kg)}}{\text{cross-sectional area (cm}^2\text{)}}$$

$$\% \text{ elongation} = \frac{\text{increase in length}}{\text{original length}} \times 100$$

The average value of five readings were taken for determining the % elongation and the results are given in Table I.

The polymeric formulations were assessed for their utility as topcoats for leather. The leathers were resin-finished and then top-finished with the new polymer formulation lacquers (1-5 in Table II). One full cross coat of the lacquers was sprayed in handling and spraying the topcoats. These products can be thinned with the usual solvents like toluene, xylene, and ethylacetate to the desired level. The treated leathers were dried and then plated at 65°C and 50 kg/cm<sup>2</sup> pressure. NC lacquer was sprayed on leather under identical conditions and kept as control. The treated samples were tested for flexing properties. From the physical testing data given in Table II, it is clear that formulation 3 gave a leather with good gloss and flexibility and it compared well with the control. Specially, these newly developed lacquers overcome the deficiencies (yellowing and cracking on aging) found in the NC lacquer-treated leathers apparently due to the migration of plasticizers in leathers.

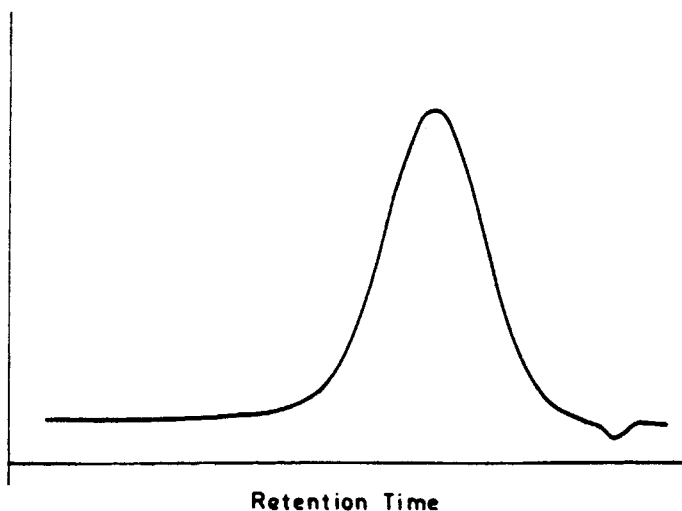
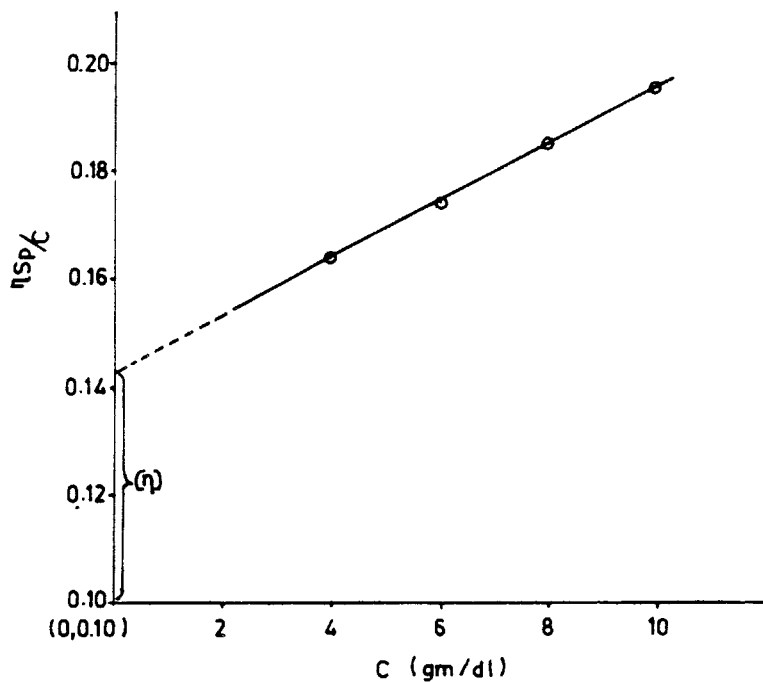


Fig. 4. Molecular weight determination of St-BA (55/45, mmol) copolymer: (a) by viscosity measurements; (b) by gel permeation chromatography.

### References

1. K. Kaleem, C. R. Reddy, S. Rajadurai, and M. Santappa, *Macromol. Chem.*, **180**, 851 (1979).
2. K. Kaleem, C. R. Reddy, and S. Rajadurai, *J. Appl. Polym. Sci.*, **26**, 2304 (1981).
3. V. Kamalakannan, S. Siddarthan, M. S. Olivannan, and S. Rajadurai, *Leather Sci.*, **30**, (7), 205 (1983).

4. B. S. R. Reddy, R. Ashady, and M. H. George, *Macromolecules*, **16**, 1813 (1983).
5. C. Pichot, M. F. Llauro, and Q. T. Pham, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 2619 (1981).
6. N. Grassie, B. J. D. Torrence, J. D. Fortune, and J. D. Gemmel, *Polymer*, **6**, 653 (1965).
7. D. A. Anderson and Eli S. Freeman, *J. Polym. Sci.*, **54**, 253 (1961).
8. J. Brandup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., Wiley-Interscience, New York, 1975.
9. J. C. Bevington, H. W. Melville, and R. P. Taylor, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 449 (1954).
10. S. Teramachi, A. Hasegawa, M. Akatsuka, A. Yamashita, and N. Takemoto, *Macromolecules*, **11** (6), 1206 (1978).
11. H. W. Melville, B. Noble, and W. F. Watson, *J. Polym. Sci.*, **4**, 629 (1949).

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