

Thermal Degradation of Poly [3-Dimethyl(methylmethacryloylethyl) Ammonium Propanesulfonate]

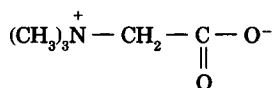
DER-JANG LIAW* and WEN-FU LEE, *Department of Chemical Engineering and Technology, National Taiwan Institute of Technology, Taipei, Taiwan 107, Republic of China*

Synopsis

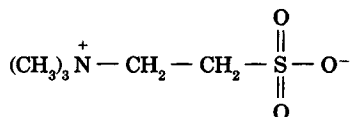
The thermal degradation of poly[3-dimethyl (methylmethacryloyl)ammonium propanesulfonate], [poly(DMAPS)], was studied under nitrogen and air atmosphere at various heating rates. The kinetic parameters such as activation energy, preexponential factor, and reaction order were determined by Ozawa's method. Thermal degradation of such polymer occurs in two and three stages in nitrogen and air atmosphere, respectively. Larger sample weights produce a larger temperature interval (ΔT), but the weight loss (ΔW) between the temperature of the start and the end of degradation is approximately independent of the sample weights.

INTRODUCTION

The internal salts of betaine substances such as carboxybetaine,



and sulfobetaine,



are widely used in the textile, medical, and other branches of industry.¹⁻¹³ 3-Dimethyl (methylmethacryloylethyl)ammonium propanesulfonate is one of the sulfobetaines and studied by several workers.^{1-3,7-10}

Szita et al. and Spriestersbach et al. reported that such monomer is polymerizable with acrylonitrile and able to apply to the dyeing processing of the textile.^{3,7} Ishikura and co-workers also used this polymerizable monomer having an amphi-ion structure to improve the physical properties of emulsion.^{8,10}

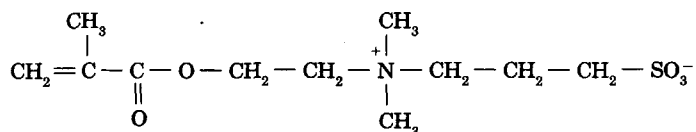
However, in the literature, no previous attempt appears to have been made to study the thermal degradation of polybetaine.

This paper will describe the results of kinetic parameters of the degradation of poly[3-dimethyl(methylmethacryloyl)ammonium propanesulfonate] [poly(DMAPS)] as well as the effect of polymer sample weight on the degradation rate, temperature interval, and weight loss.

EXPERIMENTAL

Monomer Preparation^{1,10}

In a 0.25-L volume flask equipped with a stirrer, a cooler, and a thermometer, *N,N*-dimethylaminoethyl methacrylate (8.75 g) and acetone (20 g) are charged, and the contents are stirred at 30°C. A mixture of 1,3-propane sultone (6.8 g) and acetone (3 g) is added dropwise for 30 min. After completion of the addition, the mixture is stirred at the same temperature for 4 h and then allowed to stand at room temperature for 1 week. The precipitated white crystals are collected by filtration, washed with dry acetone several times, and dried under reduced pressure to obtain 3-dimethyl(methylmethacryloylethyl)ammonium propanesulfonate having the following structure:



Yield: 14.5 g (93%); mp 280°C (lit.⁹ 280–300°C).

The monomer was characterized by elemental analysis techniques, IR and NMR. IR spectrum was taken on a Perkin-Elmer Model 735B. The ¹H-NMR spectrum was run on a JEOL Fx-100 with 3-(trimethylsilyl)-tetra-deuteriopropionic acid sodium, (CH₃)₃SiCD₂CD₂CO₂Na, as an internal standard.

Polymerization

Polymerization was thermally carried out at 60°C for 2 h. The ampoule containing 5 g monomer and 20 mL water as solvent, was evacuated several times on a high vacuum system and finally sealed off. The polymer product was precipitated with acetone, washed with water to eliminate the unchanged monomer, dried for about 24 h at 100°C under vacuum and weighed.

The conversion was about 78% and intrinsic viscosity was calculated to be 3.46 dL/g in 0.25M NaClO₄ solution with an Ubbelohde viscometer at 30°C.

Thermal Analysis

Thermal analysis was measured by Perkin-Elmer Thermal Mechanical Analyzer Model TGS-II. The heating rate at 5, 10, 20, and 40°C/min and the sample weight with 1, 2, 3, 4, and 5 mg were used.

RESULTS AND DISCUSSION

Hygroscopic Monomer

The monomer 3-dimethyl (methylmethacryloylethyl)ammonium propanesulfonate was quite hygroscopic [mp 280°C (decomposition)].

ANAL. CALC: N, 5.00%; S, 11.50%. Found: N, 4.35%; S, 11.41%.

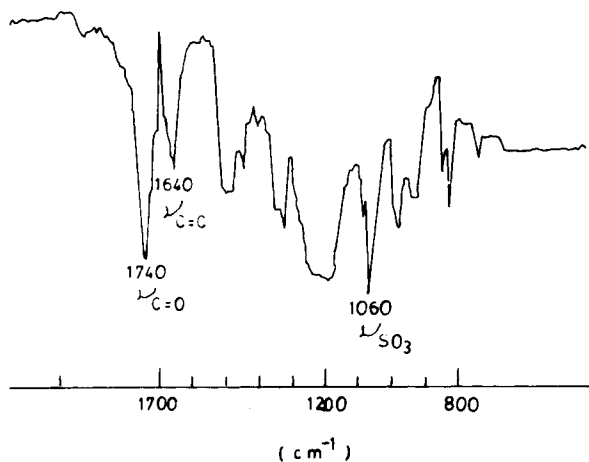


Fig. 1. IR spectrum of DMAPS.

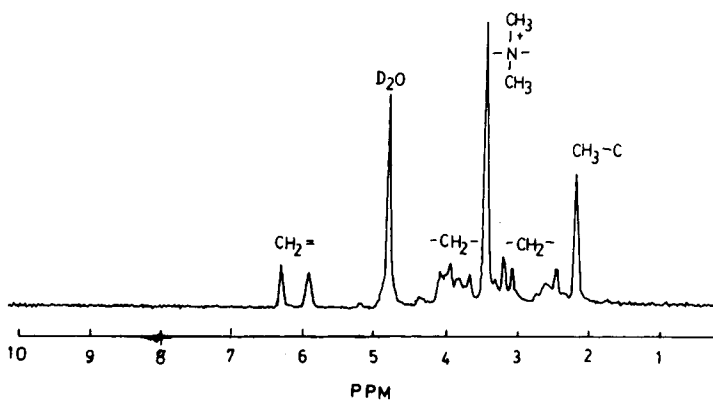


Fig. 2. $^1\text{H-NMR}$ spectrum of DMAPS (use of D_2O as solvent in 10% solution).

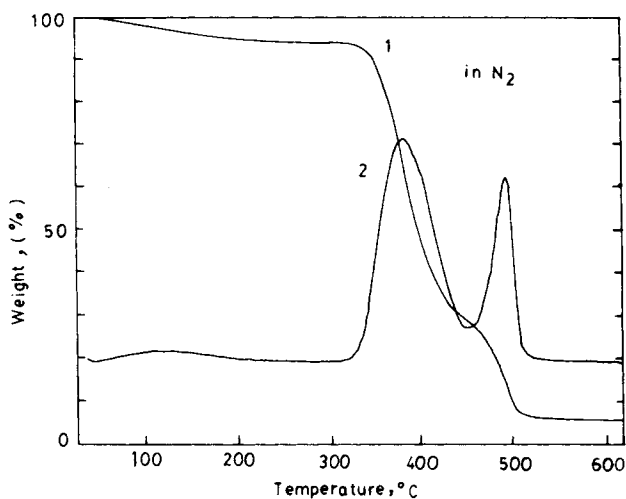


Fig. 3. The curves of 1-TGA and 2-DTG obtained during the nitrogen atmosphere degradation of poly(DMAPS).

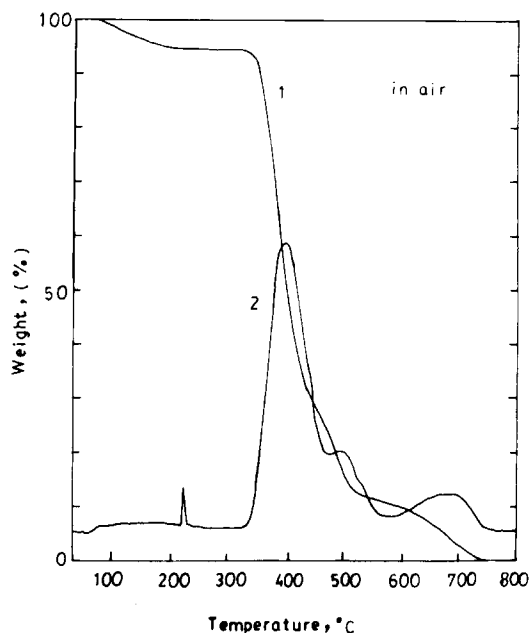


Fig. 4. The curves of 1-TGA and 2-DTG obtained during the air atmosphere degradation of poly(DMAPS).

TABLE I
Weight Loss of Degradation of Poly(DMAPS) in Nitrogen and Air Atmosphere, Heating Rate = 20°C/min

Condition	First stage		Second stage		Weight remaining (%) at 800°C
	Temperature (°C)	Weight loss (%)	Temperature (°C)	Weight loss (%)	
In N ₂	331-420	70	420-540	25	5
In air	320-435	72	435-579	17	0

TABLE II
Heat Stability of Poly(DMAPS) at Various Heating Rates in Nitrogen and Air Atmosphere

Heating rate (°C/min)	In N ₂		In air	
	T _{start} (°C)	T _{50%} (°C)	T _{start} (°C)	T _{50%} (°C)
5	300	350	305	350
10	322	374	316	360
20	331	394	320	382
40	345	415	330	394

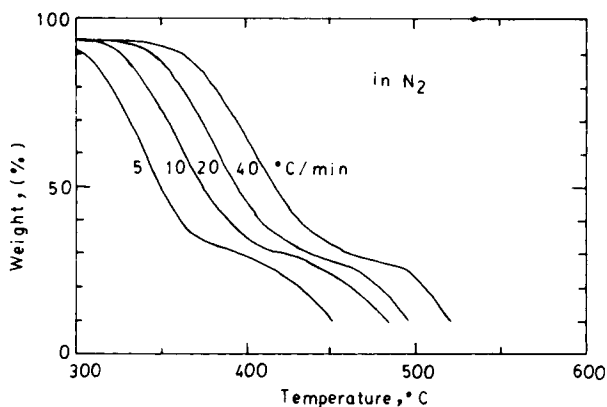


Fig. 5. TG curves of poly(DMAPS) at various heating rates in nitrogen atmosphere.

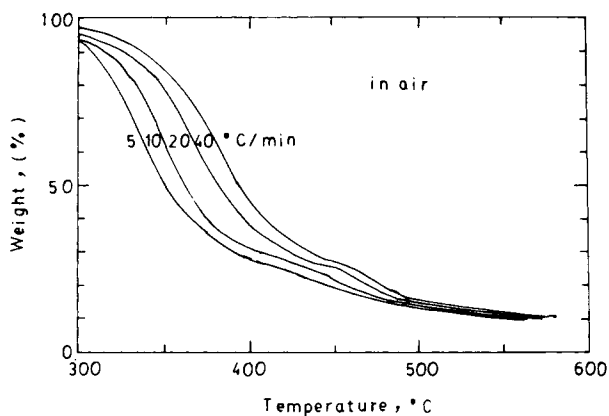


Fig. 6. TG curves of poly(DMAPS) at various heating rates in air atmosphere.

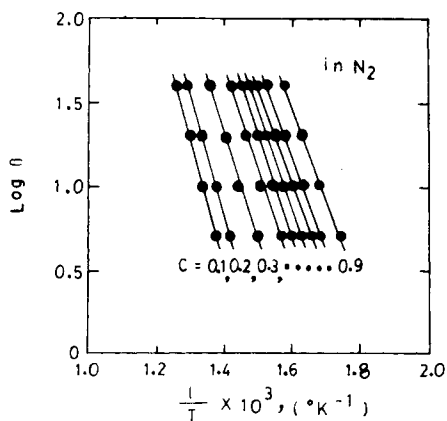


Fig. 7. The plots of logarithms of heating rate vs. the reciprocal absolute temperature for indicated conversions of the degradation of poly(DMAPS) in nitrogen atmosphere.

The hygroscopicity of monomer hinders the analysis. This phenomenon was also observed in other literatures reported previously.^{11,14}

The structure of the monomer was further characterized by IR and NMR as shown in Figures 1 and 2, respectively.

TG Curve Characteristics of Poly(DMAPS)

The TG curves for the thermal degradation of a 5-mg poly(DMAPS) sample are shown in Figures 3 and 4 with the heating rate of 20°C/min in nitrogen and air atmospheres, respectively. From Figures 3 and 4 it can be seen that thermal degradation of such polymer occurs in two and three stages under nitrogen and air atmospheres, respectively. These phenomena may be due to the formation of a more thermally resistant char which occurs with approximately 30% of the initial sample weight by 420°C.¹⁵

The TG curve for poly(DMAPS) in nitrogen atmosphere has two stages and shows two maximum peaks at 380 and 490°C. In the first stage, weight loss starts at 331°C and continues to 420°C with 70% weight loss. The second stage (25%) is complete by 540°C and shows a maximum rate of weight loss at 490°C shown by derivative equipment associated with TG apparatus. The weight percentage remaining at 800°C is 5%.

However, the TG curve for poly(DMAPS) in air atmosphere has three distinct stages and shows three maximum peaks at 380, 490, and 690°C. In the first stage, weight loss starts at 320°C and continues to 435°C with 72% weight loss and shows a maximum rate of weight loss at 380°C. The second stage (17%) is complete by 579°C. The third stage (11%) is complete by 742°C, and no ash is left.

Table I shows the percentage weight loss of poly(DMAPS) in nitrogen and air atmosphere and the corresponding temperature at the heating rate of 20°C/min.

As criterion of heat stability of the polymer, we take the temperature of the start of intense degradation (T_{start}) and the temperature corresponding to a 50% weight loss ($T_{50\%}$) at various heating rates. The results are presented in Table II. From Table II, it is clear that the temperature of thermal degradation of poly(DMAPS) in air is lower than in nitrogen at higher heating rate.

Determination of Kinetic Parameters for the Thermal Degradation of Poly(DMAPS)

The results of the thermogravimetry at various heating rates in nitrogen and air atmosphere are plotted against the absolute temperature in Figures 5 and 6, respectively.

The activation energy was determined by Ozawa's method for a given value of weight fraction ($W\%$).¹⁶ He reported that the weight decreases to a given fraction at the temperature T_1 , for the heating rate of β_1 , at T_2 for β_2 , and so on. The following equation could be derived:

$$-\log \beta_1 - 0.457 \frac{E_1}{RT_1} = -\log \beta_2 - 0.457 \frac{E_2}{RT_2} \quad (1)$$

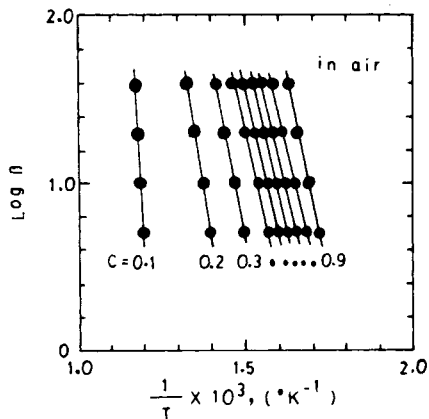


Fig. 8. The plots of logarithms of heating rate vs. the reciprocal absolute temperature for indicated conversions of the degradation of poly(DMAPS) in air atmosphere.

TABLE III
Activation Energies and Preexponential Factors of the Degradation of Poly(DMAPS) in Nitrogen and Air Atmosphere

Condition	First stage		Second stage	
	ΔE (kJ/mol)	$\log A^a$	ΔE (kJ/mol)	$\log A^a$
In N_2	103.3	8.88	126.7	8.91
In air	154.8	12.38	222.6	15.96

^a A is calculated by Ozawa's method.¹⁶ The dimension of A is min^{-1} .

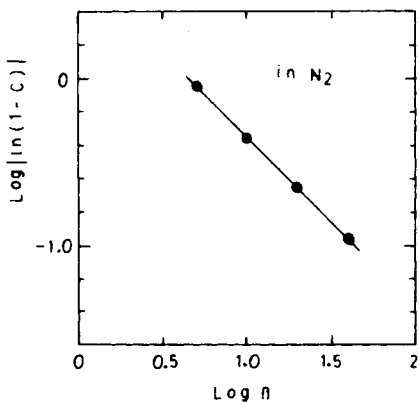


Fig. 9. Relationship obtained by Ozawa's method for $n=1$ in nitrogen atmosphere.

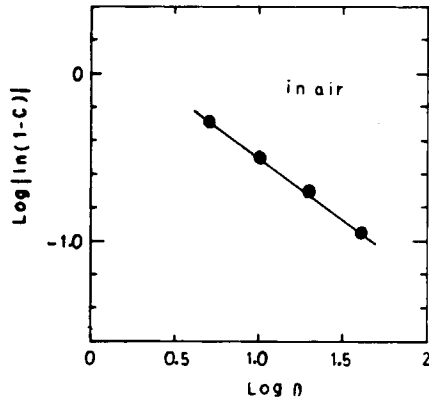


Fig. 10. Relationship obtained by Ozawa's method for $n=1$ in air atmosphere.

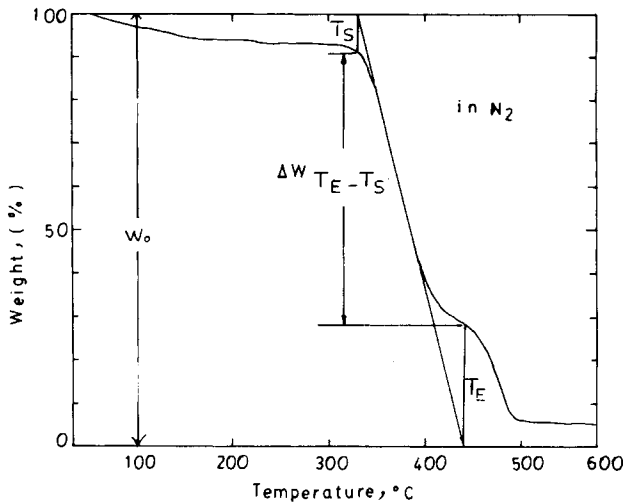


Fig. 11. Example of TGA thermogram of poly(DMAPS) with definition of temperature of the start (T_S) and the end (T_E) of degradation, weight loss (ΔW), and total weight loss (W_0).

TABLE IV
Definition of Variables and Constant

ΔW	$= (W/W_0) \times 100$	(%)
ΔT	$= T_E - T_S$	
\bar{V}	$= \Delta W / \Delta T$	
W_0	initial weight	(%)
W	weight loss between T_E and T_S	(%)
ΔW	weight change between T_E and T_S	(%)
T_S	extrapolated temperature at start of the first stage degradation	(°C)
T_E	extrapolated temperature at end of the first stage degradation	(°C)
\bar{V}	average specific rate of degradation	(%/°C)

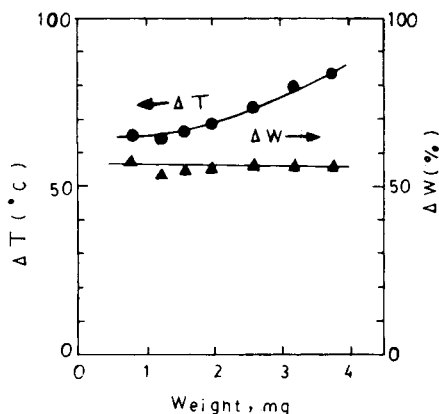


Fig. 12. Effect of sample weight on temperature interval ΔT and weight loss ΔW ; heating rate = $20^{\circ}\text{C}/\text{min}$.

where E is the activation energy and R is the ideal gas constant. From Figures 5 and 6, the logarithms of the heating rates could be plotted against the reciprocal absolute temperature, until which point the weight of the sample decreases to a given fraction. The results are shown in Figures 7 and 8. Straight lines are drawn by the method of the least squares. From these lines the activation energies are determined as listed in Table III in nitrogen and air.

The kinetic order of the reaction could be derived by use of eq (3)^{16,17}:

$$\log|(1-C)^{1-n} - 1| = \log \beta \quad (n \neq 1) \quad (2)$$

$$\log|\ln(1-C)| = \log \beta \quad (n=1) \quad (3)$$

The conversion C is defined by

$$C = 1 - W/W_0 \quad (4)$$

where W_0 and W represent initial weight and weight at any time, respectively, and n is the reaction order. The logarithm of $\ln(1-C)$ can be plotted

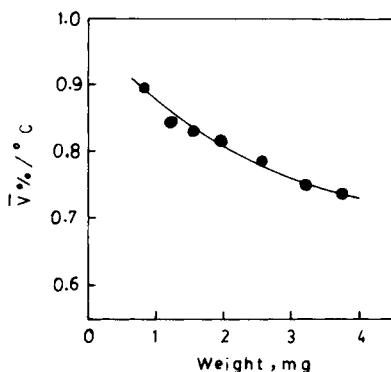


Fig. 13. Effect of sample weight on average specific rate of degradation, \bar{V} ; heating rate = $20^{\circ}\text{C}/\text{min}$.

against the logarithm of heating rate (β) in nitrogen and air atmosphere as shown in Figures 9 and 10, respectively. From Figures 9 and 10, the good linear relation was obtained. These results mean that the kinetic order is one in both conditions.

Effect of Sample Weight on Degradation Rate (\bar{v}), Temperature Interval (ΔT), and Weight Loss (ΔW)

An example of TGA thermogram of poly(DMAPS) is shown in Figure 11. The TG curve contains all the information necessary to calculate the average specific rate of weight loss (\bar{v}), the temperature interval of the degradation (ΔT), and the weight loss (ΔW).

The definitions of the Figure 11 are listed in Table IV. A poly(DMAPS) was used to investigate the influence of sample weight at a constant heating rate of 20°C/min in nitrogen on ΔW and ΔT . The result is plotted in Figure 12, which shows that larger sample weights produce a larger ΔT . However, the ΔW is approximately independent of the sample weights.

Figure 13 shows that higher sample weight decreases the rate of degradation of this polymer. This result was also observed by Newkirk,¹⁸ Coats and Redfern,¹⁹ and Kokta et al.²⁰

References

1. Rohm and Hass Co., Neth. Pat. Appl. 6411736 (1965).
2. E. I. Du Pont de Nemours and Co., Neth. Pat. Appl. 6409012 (1965).
3. J. Szita, U. Bahr, H. Wieden, H. Marzolph, and G. E. Nischk, Belg. Pat. 659316 (1965).
4. J. Szita, U. Bahr, H. Wieden, and G. E. Nischk, Ger. Pat. 1,211,156 (1966).
5. J. Szita, U. Bahr, H. Wieden, H. Marzolph, and G. E. Nischk, Br. Amended Pat. 1,024,029 (1966).
6. J. Szita, U. Bahr, H. Wieden, H. Marzolph, and G. E. Nischk, U.S. Pat. 3,478,001 (1969).
7. D. R. Spriestersbach, R. A. Clarke, M. Couper, and H. T. Patterson, U.S. Pat. 3,473,998 (1969).
8. R. Mizuguchi, S. Ishikura, A. Takahashi, and A. Uenaka, U.S. Pat. 4,215,028 (1980).
9. C. M. Samour and M. L. Falxa, U.S. Pat. 3,671,502 (1972).
10. S. Ishikura, R. Mizuguchi, and A. Takashashi, Japan Kokai 80,386 and 80,387 (1977).
11. T. A. Asonova, Ye. F. Razvodovkii, A. B. Zezin, and V. A. Kargin, *Dokl. Akad. Nauk SSSR*, **118**,583 (1969).
12. T. A. Asonova, Ye. F. Razvodovkii, and A. B. Zezin, *Vysokomol. Soyed.*, **A16**, 777 (1974).
13. D. A. Topchiev, L. A. Mkrtychyan, R. A. Simonyan, M. B. Lachinov, and R. A. Kabanov, *Vysokomol. Soyed.*, **A19**, 506 (1977).
14. H. Ladenheim and H. Morawetz, *J. Polym. Sci.*, **26**, 251 (1957).
15. D. A. Chatfield, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 1681 (1983).
16. T. Ozawa, *Bull. Chem. Soc. Jpn.*, **38**, 1881 (1965).
17. H. Nishizaki, K. Yoshida, and J. H. Wang, *J. Appl. Polym. Sci.*, **25**, 2869 (1980).
18. A. E. I. Newkirk, *Anal. Chem.*, **32**, 1568 (1960).
19. A. W. Coats and J. D. Redfern, *Analyst.*, **88**, 906 (1963).
20. B. V. Kokta, J. L. Valade, and W. N. Martin, *J. Appl. Polym. Sci.*, **17**, 1 (1973).

Received December 3, 1984

Accepted February 1, 1985