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COMPARATIVE STUDIES OF CASTOR AND HYDROGENATED CASTOR OIL URETHANE/PMMA SEMI AND FULL INTERPENETRATING POLYMER NETWORKS

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Key Words: Castor Oil, Hydrogenated Castor Oil, Urethane, Interpenetrating Polymer Networks (IPNs), Poly(methyl methacrylate)

ABSTRACT

Semi and full interpenetrating polymer networks (IPNs) of castor oil and hydrogenated castor oil urethane and poly(methyl methacrylate) were synthesized by the sequential mode of synthesis. These IPNs were characterized for their physicomechanical properties, swelling properties, and thermal behavior. The glass transition temperatures (T_gs) were determined by differential scanning calorimetry (DSC). The variation in the blend ratio resulted in drastic changes in the % elongation at break, whereas, nominal changes were observed in the tensile strength values. Interestingly, the semi-IPNs exhibited higher tensile strength and density but lower elongation than the corresponding full IPNs. From glass transition temperature measurements it was observed that full-IPNs showed single T_g value, whereas, semi (IPNs exhibited two T_g values corresponding to their respective homopolymers. In the case of swelling behavior, the castor oil urethane and PMMA IPNs offered relatively more solvent resistance than hydrogenated castor oil /PMMA.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are the special type of chemical combinations of different polymer networks in which permanent entanglements, with essentially no chemical bonds between them, are formed by simultaneous or sequential crosslinking of the parent networks. The multicomponent system thus obtained displays a broad range of properties from toughened elastomers to high impact plastics. The physical nature of the constituent networks, their proportion in the blend, etc., control the ultimate performance of the resulting IPNs [1-2].

Even though castor oil based polyurethanes and their IPNs have been studied by many authors [3-6], no detailed information is available on the systems based on hydrogenated castor oil. In the present work, attention is focused particularly on the study of the variation in the properties of castor oil when the double bonds in the castor oil chains were saturated. Hence, the present paper deals with the syntheses and characterization of polyurethanes from both the castor oil, and hydrogenated castor oil and their corresponding full and semi IPN's using polymethyl methacrylate as the plastic component. These IPNs have been studied for their physicomechanical and thermal properties, and compared with that of the unmodified castor oil based polyurethane and their respective IPNs.

EXPERIMENTAL

Materials

British Standard Specifications (BSS) grade castor oil [acid value, 2.0 mg KOH/g, hydroxyl value 162 mg KOH/g and iodine value (wij method) 82-90] and Hydrogenated castor oil [acid value, 2.0 mg KOH/g, hydroxyl value 162 mg KOH/g, iodine value (wij method) 2-5 and melting point 82-86°C] were procured from M/s Jayant Oil Mill (India),and their characteristic properties are given in Table 1. Isophorone diisocyanate (IPDI) and benzoyl peroxide were obtained from Fluka Switzerland) and Thomas Baker Co., (India), respectively. Methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) purchased from Sisco-Chem (India) and Fluka (Switzerland), respectively, were washed initially with 2% NaOH, followed by distilled water and then dried over $CaCl_2$. Finally, they were distilled under reduced pressure prior to use. Dibutyltin dilaurate (DBTL) was obtained from the local market. All other reagents were of analytical grade and have been used without further purification.

TABLE 1. Mechanical and Physical Properties of Homopolymers and IPNs

	Composition PU/ PMMA wt%	Tensile strength MPa	Elongation at break %	Hardness Shore A
Homopolymers				
[a]CU	100/ 0	1.8	207	72
[b]HCU	100/ 0	2.3	228	86
PMMA	0/ 100	62.0	8	hard
Full- IPNs				
CU / PMMA	25/ 75	2.3	20	90
CU/ PMMA	50/ 50	1.7	45	76
CU/PMMA	75/ 25	1.3	140	71
HCU/PMMA	25/ 75	3.0	25	100
HCU/PMMA	50/ 50	2.2	60	96
HCU/PMMA	75/ 25	1.6	165	92
Semi- IPNs				
CU/PMMA	25/ 75	3.7	15	90
CU/PMMA	50/ 50	2.5	33	88
CU/PMMA	75/ 25	1.9	92	86
HCU/PMMA	25/ 75	4.2	18	100
HCU/PMMA	50/ 50	2.8	43	92
HCU/PMMA	75/ 25	2.1	96	88

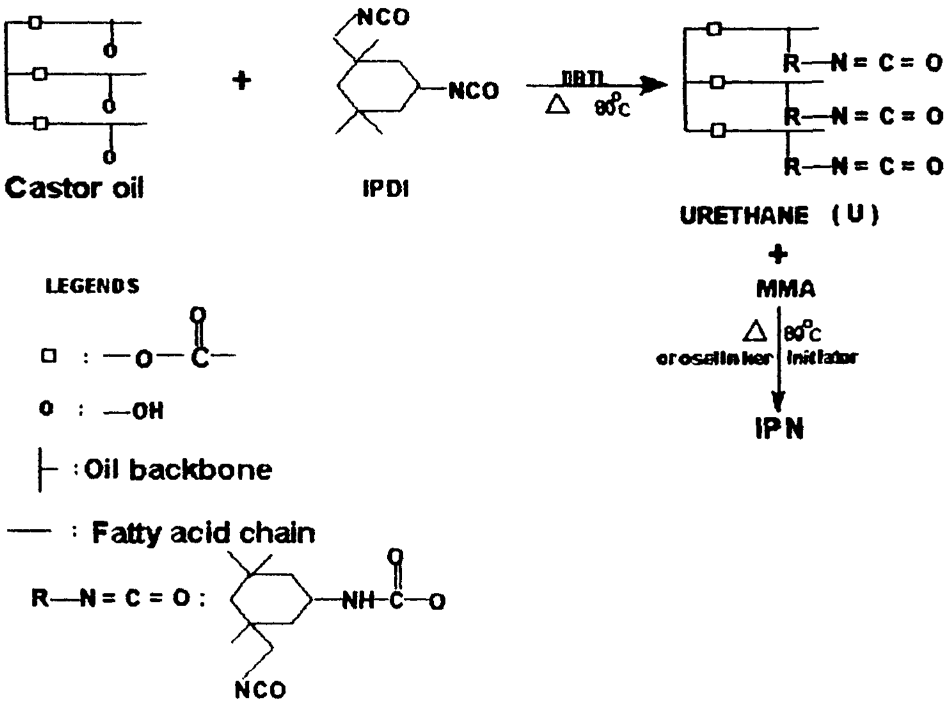
[a]CU = castor oil urethane

[b]HCU= hydrogenated castor oil urethane

Syntheses

Urethane Networks [Castor Oil Urethane (U) and Hydrogenated Castor Oil Urethane (HCU)]

A reaction kettle, equipped with stirrer and nitrogen inlet, was charged with one equivalent of 50% solution of castor oil/hydrogenated castor oil in dioxane, followed by the addition of two equivalents of IPDI along with the catalyst DBTL (0.01 g/g of IPDI) and kept in a thermostated water bath. The temperature was then raised to 80 ± 2°C and was maintained for 2 hours with continuous stirring. After the completion of 2 hours, triethanolamine (1.0 wt% of the resin for chain extension and curing) was added and mixed thoroughly for 5 minutes. The solution was then poured into the mold, where it was kept initially at 80°C for 24 hours and then at 120°C for 4 hours.



Scheme 1. Synthesis of Urethane and IPNs

Interpenetrating Polymer Networks (IPNS): (Scheme 1)

Full IPNs

The reaction kettle containing urethane prepolymer was charged with triethanolamine (1.0 wt% based on urethane), predetermined amount of MMA along with EGDMA (1.0 wt% based on MMA) and benzoyl peroxide (0.5 wt% based on MMA) and was intimately mixed for 3 minutes at 40°C. The temperature was then raised to 75 to 78°C and the reaction was further continued for 60 minutes. The reaction mixture was then poured into the mold and cured initially at 75 to 78°C for 24 hours and later on at 120°C for 6 hours.

Semi-IPNs

Semi-IPNs were prepared in the same manner as described in the case of full-IPNs, except that the EGDMA crosslinker for MMA) was not added in the reaction mixture.

Characterizations

Infrared spectra of the semi and full IPN's were obtained on a Shimadzu FTIR 4200 series spectrophotometer using KBr pellets, whereas, in the case of urethane prepolymer, which was thick and syrupy in nature, a thin film was cast over NaCl block. Tensile strength and elongation were measured using a computerized tensile testing machine "Tensilon" (R & D Electronics, India) as per ASTM D 638 standard, and the hardness was determined with the Shore A durometer using ASTM D 2240-75 standard. The apparent densities of the films were obtained by weighing strips of the film of measured volume [7]. The swelling study was carried out in water, methyl ethyl ketone (MEK) and toluene [8]. Thermogravimetric measurements were made on a Mettler TA 4000 thermogravimetric analyzer (TGA) at a heating rate of 10°C/min. in nitrogen atmosphere and then the activation energy was computed by using Broido's method [9]. The glass transition temperatures were determined by differential scanning calorimetry on DuPont 9900 thermal analyzer at a heating rate of 10°C/min in nitrogen atmosphere.

RESULTS AND DISCUSSION

Infrared Spectroscopy (IR)

IR spectra of urethane prepolymer showed the characteristic absorption bands at 1740 cm^{-1} and 3400 cm^{-1} corresponding to urethane and amide II (-NH stretching) respectively. As the prepolymer is isocyanate terminated, an intense and sharp band due to NCO is observed at 2270 cm^{-1}. IR spectra of the semi and full IPN's showed all the bands corresponding to urethane and methacrylate network and did not show the appearance of any additional bands, thereby ruling out the possibility of any chemical interaction between the component networks.

Mechanical Properties

The tensile strength and elongation at break data of the IPNs and their component networks are shown in Table 1. In all cases, a minimum in the tensile strength was observed at 75% polyurethane, and a maximum at 25% polyurethane. It can be noted from Table 1 that the tensile strength increased and elongation at break decreased with a corresponding decrease in the polyurethane content in the IPNs. Furthermore, it was found that the variation of blend ratio resulted in drastic changes in the elongation, whereas, nominal changes were observed in the tensile strength. Comparing the tensile strength and elongation of castor oil urethane (CU) and hydrogenated castor oil urethane (HCU) and their IPNs using Poly(methyl methacrylate) (PMMA) as a second component, it was found that HCU/PMMA IPNs showed superior mechanical properties over that of CU and CU/PMMA IPNs. In addition, on inspection of Table 1, it was found that semi-IPNs exhibited higher tensile strength and lower elongation than the corresponding full-IPNs. This can be explained by considering the fact that the soft and elastomeric polyurethane moieties have much higher free volume. This results in ample scope for threading of polyurethane with PMMA networks in the case semi- IPNs, where the chains are linear and have greater mobility. On the other hand, in the case of full- IPNs, the high degree of crosslinking lowers the statistical probability of threading (easy mobility of entangled chains), thereby precluding the reinforcement effect of interpenetration. Interestingly, during tensile strength measurements, all the semi-IPNs were observed to stress whiten, indicating failure arising from crazing mechanism, whereas, in the case of full-IPNs this phenomenon was not observed, because of the improved compatibility of urethane and PMMA.

Hardness (Table 1) data revealed that the hardness increased with the corresponding increase in the PMMA concentration in the IPNs, which is due to the fact that soft and flexible urethane resin was being substituted by poly (methyl methacrylate), which is hard. On further inspection of Table 1, it was found that HCU/PMMA IPNs exhibited greater hardness than those of CU/PMMA IPNs, possibly due to the formation of more crosslinked network by the former. Interestingly, the semi-IPNs showed greater hardness than the full-IPNs, because in the case of semi IPNs due to partial mixing of the hard PMMA phase with soft PU phase, only some part of PMMA gets interpenetrated, whereas, the remaining uninterpenetrated PMMA behaves like a filler.

Apparent Density

The density-composition curve of IPNs (Figures 1 and 2) showed that the densities of both the semi and full IPNs increased with the corresponding increase in the PMMA contents. PMMA is denser than urethane, and hence, the density of IPN system increased as more and more PMMA was substituted. Interestingly, it was observed that the density-composition curve of CU/PMMA semi and full IPNs (Figure 1) were below that of the corresponding curves representing the theoretical densities (based on the volume additivity principle which

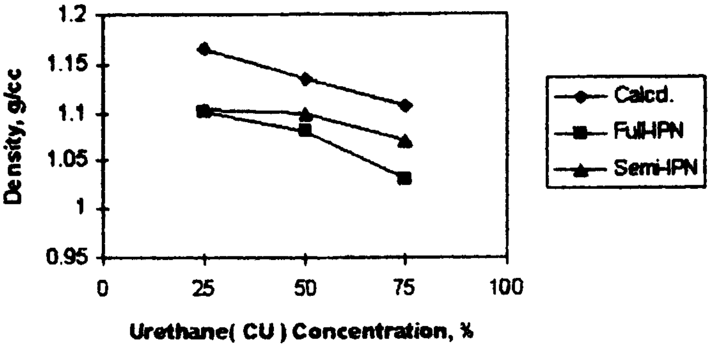


Figure 1. Density vs Polyurethane concentration (in wt%) of castor oil urethane/PMMA Semi and full IPNs.

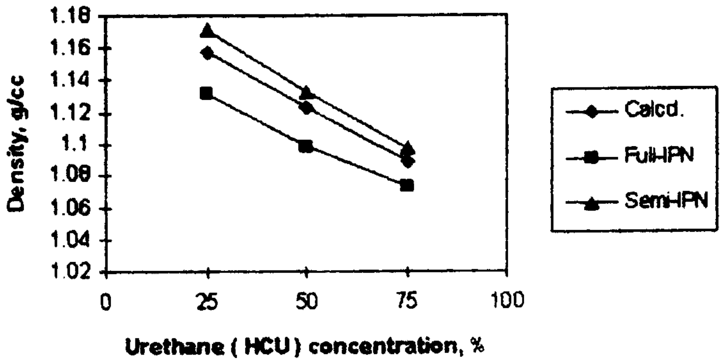


Figure 2. Density vs Polyurethane concentration (in wt%) of hydrogenated castor oil urethane/PMMA Semi and full IPNs.

states that [$d=w_1d_1+w_2d_2$] where, d is the density of the IPN sample, w_1 and w_2 are the weight fractions of the constituents, d_1 and d_2 are the corresponding densities, respectively [2]). However, in the case of HCU/PMMA IPNs system (Figure 2), the density curve for full IPNs was situated below, whereas, for the semi IPNs it was above that of the calculated curve. This can be explained by considering the fact that some of the "holes" in the comparatively loosely packed amorphous urethane structure were filled up by the self entanglement of the growing network [11]. Furthermore, Figures 1and 2 revealed that the IPNs from HCU/ PMMA showed higher density than the corresponding IPNs of CU/PMMA indicating relatively greater extent of interpenetration in the former.

TABLE 2. Swelling of Homopolymers and IPNs

Sample code	Composition PU/PMMA wt %	% Swelling			
Homopolymers		MEK		Toluene	
		Exp.	Calcd.[c]	Exp.	Calcd.[c]
[a]CU	100/ 0	96	-	111	-
[b]HCU	100/ 0	98	-	122	-
PMMA	0/ 100	100	-	95	-
Full- IPNs					
CU/PMMA	25/ 75	98	99	104	99
CU/PMMA	50/ 50	103	98	118	103
CU/PMMA	75/ 25	110	97	121	107
HCU/PMMA	25/ 75	103	100	115	102
HCU/PMMA	50/ 50	113	99	127	108
HCU/PMMA	75/ 25	120	99	178	115
Semi- IPNs					
CU/PMMA	25/ 75	128	99	145	99
CU/PMMA	50/ 50	142	98	172	103
CU PMMA	75/ 25	121	97	190	107
HCU/PMMA	25/ 75	139	100	156	102
HCU/ MMA	50/ 50	160	99	224	108
HCU/PMMA	75/ 25	187	99	235	115

[a]CU: castor oil urethane

[b]HCU: hydrogenated castor oil urethane

[c]Calcd: calculated swelling (wt%) = $W_1 S_1 + W_2 S_2$; W_1, W_2 are the weight fractions and S_1, S_2 are the swellings of urethane and PMMA respectively

Swelling Study

The 24 hour swelling ratios, along with the theoretical ratios of the component networks for comparison, are presented in Table 2. In all the cases, swelling was more prominent in toluene than in methyl ethyl ketone (MEK). In both the solvents, full and semi-IPNs showed slightly greater swelling than the theoretical swelling of the parent networks. Further, the swelling of the semi-IPNs in toluene and MEK was greater than that of the corresponding full-IPNs. This is because the semi-IPN networks are loosely packed since the solvent can easily penetrate into the core of the matrix. Furthermore, it was evident from

TABLE 3. Glass TransitionTemperatures (T_gs) of Homopolymers and IPNs

Sample code	Composition PU/PMMA wt %	No. of T_gs	T_g (degree Kelvin)
Homopolymers			
[a]CU	100/0	1	244
[b]HCU	100/0	1	236
PMMA	0/100	1	382
Full- IPNs			
CU/PMMA	25/75	1	343
CU/PMMA	50/50	1	313
CU/PMMA	75/25	1	283
HCU/PMMA	25/75	1	340
HCU/PMMA	50/50	1	309
HCU/PMMA	75/25	1	277
Semi-IPNs			
CU/PMMA	25/75	2	247, 374
CU/PMMA	50/50	2	252, 370
CU/PMMA	75/25	2	250, 373
HCU/PMMA	25/75	2	239, 376
HCU/PMMA	50/50	2	240, 375
HCU/PMMA	75/25	2	242, 377

[a] CU= castor oil urethane

[b] HCU= hydrogenated castor oil urethane

Table 2 that swelling increased with a corresponding increase in the concentration of urethane in the IPNs. Finally, it is interesting to note that both the semi and full IPNs of CU/PMMA showed more resistance to swelling than the corresponding semi and full IPNs of HCU/PMMA.

Glass Transition Temperatures (T_gs)

Glass transition temperatures of the semi and full IPNs are listed in Table 3. The lower T_g values correspond to the polyurethane phase transition, and the higher T_g values correspond to the PMMA phase transition. All the full IPNs,

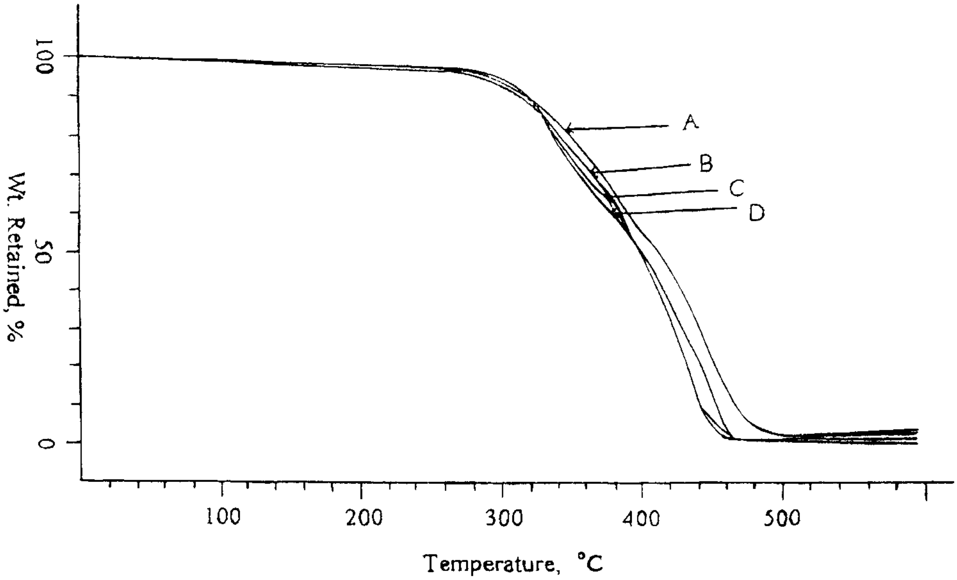


Figure 3. Representative thermograms of CU/PMMA and HCU/PMMA Semi and Full IPNs, A: Full IPN (CU50/PMMA50), B: Semi IPN (CU50/PMMA50), C: Full IPN (HCU50/PMMA50), D: Semi IPN (HCU50/ PMMA50).

except HCU/PMMA (25/75) IPN, showed single glass transition indicating one phase morphology, whereas, all the CU/PMMA and HCU/PMMA semi IPNs exhibited two glass transition temperatures suggesting a heterophase morphology. However, the slight inward shift of T_gs gave an evidence that the extent of interpenetration taking place between urethane and poly(methyl methacrylate) was low. Furthermore, it is difficult to correlate the composition of IPNs with the shifting in T_gs because of the wide distribution of phase domain sizes and the complexity of the morphology.

Thermal Properties

Thermal behavior of the semi and full IPNs, and that of the corresponding homopolymers suggests that, the thermal stability of the IPNs falls intermediate between those of the urethane and PMMA. Clustering of the IPNs curves [Figure 3] indicated that there was no significant difference in their degradation behavior. However, from the activation energy data [Table 4] it was evident that the castor oil urethane and their corresponding semi and full IPNs were relatively more stable in the first stage of degradation than the

TABLE 4. Thermal Decomposition of Homopolymers and IPNs

Sample code	Compositions	Decomposition stages			
	PU/PMMA (wt%)	Stage I (°C)	Activation Energy (kcal/mol) E*	Stage II (°C)	Activation Energy (kcal/ mol) E*
[a]CU	100/0	254-391	36	391-502	44
[b]HCU	100/0	217-367	21	367-500	44
PMMA	0/100				
Full IPNs					
CU/PMMA	50/50	194-365	29	365-562	40
HCU/PMMA	50/50	305-500	19	-	-
Semi IPNs					
CU/PMMA	50/50	240-390	36	390 -505	40
HCU/PMMA	50/50	194 -364	24	364-500	43

[a] CU= castor oil urethane

[b] HCU= hydrogenated castor oil urethane

hydrogenated castor oil urethane (HCU) and their corresponding IPNs. In all the cases, except PMMA, generally, a two stage decomposition pattern was observed. Stage I corresponding to the urethane bond breaking, occurred in the temper-ature range 330-340°C. Stage II, the polyol decomposition, occurred at around 450-455°C for polyurethane and, in the case of IPNs, Stage I included both urethane bond breaking as well as unzipping of PMMA [10]. Finally, polyurethanes showed complete weight loss at 500°C and the IPN's at 550°C. An investigation of thermograms indicated that, all the IPNs decomposed within 2-4% weight loss in the temperature range of 0-200°C, and about 10% weight loss occurred at 310°C-320°C. There was a rapid weight loss from 30-90% in the temperature range of 355°C-475°C probably due to the decrosslinking of the two networks, and almost all the IPNs decomposed completely from 475°C onwards up to 550°C. In this region, along with the unzipped MMA monomer, the polyol of the urethane network might have most probably been detached by free radical mechanism. For all the homopolymers and the IPN's activation energy values were lower in the first stage and higher in the second stage indicating that, the degradation process was relatively faster in the first stage than in the second stage. Finally, the PMMA alone showed single stage decomposition and lower activation energy, indicating that the chain scission of PMMA was a rapid process.

CONCLUSION

Based on the comparison of castor oil and hydrogenated castor oil urethane and their IPNs using poly(methyl methacrylate) as plastic component, it can be noted that, the saturation of the double bond in the castor oil has resulted in the enhancement of the mechanical properties and the thermal stability in early stage of degradation. Along with glass transition behavior, swelling studies can also effectively provide more detailed information about the extent of interpenetration. However, both the polymers were highly transparent and thus showed good compatibility.

REFERENCES

[1] H. X. Xiao, K. C. Frisch, and H. L. Frisch, *J. Polym. Sci., Polym. Chem., Ed., 22,* 1035 (1984).

[2] Chakrabarty and B. Das, *J. Appl. Polym. Sci., 60,* 2125 (1996).

[3] G. M. Yenwo, J. A. Manson, J. Pulido, L. H. Sperling, A. Conde, and N. Devia, *J. Appl. Polym. Sci., 21,* 1531 (1977).

[4] L. H. Sperling, "Interpenetrating Polymer Networks and Related Materials", Plenum Press, New York, (1981).

[5] P. Patel and B. Suthar, *Polymer, 31,* 339 (1990).

[6] Vilas Athawale and Suresh Kolekar, *Eur. Polym. J.* (in press).

[7] H. L. Frisch, D. Klempner, and K. C. Frisch, *Polym. Lett. 7,* 775 (1969).

[8] L. H. Sperling and E. N. Mihalakis, *J. Appl. Polym. Sci., 17,* 3811 (1973).

[9] A. Broido, *J. Polym. Sci., Polym. Phy. Ed., 7,* 1761 (1969).

[10] P. D. Nair and M. Jayabalan , *J. Polym. Sci., Polym. Chem. Ed., 28,* 3775 (1990).

[11] R. Millar, *J. Chem. Soc.*, 1311 (1960).

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