

Preparation and properties of poly (α -methyl- α -ethyl- β -propiolactone)

Denis Duchesne and Robert E. Prud'homme

Groupe de recherche sur les macromolécules, Département de chimie, Université Laval, Québec 10, P.Q., Canada G1K 7P4

Poly (α -methyl- α -ethyl- β -propiolactone) (PMEPL) has been prepared by anionic polymerization. PMEPL is a semi-crystalline polymer having a melting point of 393 K, a glass transition temperature of 260 K and a low degree of crystallinity. It presents upon stretching an $\alpha \rightarrow \beta$ transition which is reversible upon annealing, and which is quite similar to the α - β transition found in other polylactones. Its dynamic mechanical properties show a β relaxation peak at 290 K, and indicate the presence of a γ relaxation region around 120 K.

INTRODUCTION

Among the different polymers which can be derived from α - α -disubstituted- β -propiolactones, the dimethyl derivative, commonly called polypivalolactone (PPL), is certainly the one that has produced the greater interest.^{1,2} However, because of several problems partly related to its high degree of crystallinity, it has not reached so far the stage of commercial exploitation. The recent trend is then to incorporate PPL into a copolymer where the second component is a less crystalline material: it can be an elastomer³⁻¹¹ or another polylactone.¹²⁻¹⁴ In the latter case, poly (α -methyl- α -*n*-propyl- β -propiolactone) (PMPPL)^{12,13} and poly (α -methyl- α -*n*-butyl- β -propiolactone) have been used.¹⁴ But other derivatives of the same series can certainly also be used.

From another point of view, it is known that PPL presents a so-called α - β transition, which is a crystal-crystal transformation, where the α phase is characterized by a 2_1 helical conformation and the β phase by a fully extended planar zig-zag conformation.¹⁵⁻¹⁹ This transition is also known to occur in the unsubstituted poly (β -propiolactone) (P β L)²⁰⁻²² and in PMPPL.^{23,24} In all cases, the transition is reversible: the β phase is induced by stretching the sample and the α phase is recovered by annealing. The transition probably occurs in other members of the same polylactone series.

It then seems interesting to study homopolymers of the same series in order to be able to prepare additional copolymers with PPL and to verify the generality of the α - β transition in polylactones. The present paper aims to report the preparation and properties of poly (α -methyl- α -ethyl- β -propiolactone) (PMEPL). Results will be presented concerning its thermal behaviour, its crystal structure stability and its dynamic mechanical properties.

EXPERIMENTAL

PMEPL was prepared by anionic polymerization of the α -methyl- α -ethyl- β -propiolactone by using tetraethylammonium benzoate as initiator. The polymerization was conducted at 44°C, in tetrahydrofuran, and under nitrogen

atmosphere. The monomer was prepared from 2-ethyl-2-methyl-1, 3-propane-diol using a classical procedure.^{12,13} The initiator was recrystallized under inert atmosphere from an ethyl acetate-*n*-butanol 100:1 mixture before polymerization.

The polymerization had a living character since the molecular weights of the polymers could be predicted by the molar ratio of the monomer to the initiator. Three different samples have been prepared. Their intrinsic viscosities, measured in methylene chloride at 30.55°C, were 0.20, 0.55 and 0.95 g dl⁻¹. Their molecular weights, obtained by gel permeation chromatography, in tetrahydrofuran at 25°C, were, respectively, 10 000, 80 000 and 200 000 gmol⁻¹. All results presented herein have been taken from the 80 000 gmol⁻¹ sample, except the nuclear magnetic resonance (nmr) spectrum which was taken from the 10 000 gmol⁻¹ polymer. The PMEPL was soluble only in tetrahydrofuran, ethylene chloride, *m*-cresol, trifluoroacetic acid and ortho-dichlorobenzene (ODCB). But in most of these solvents, only small concentrations were possible and these occurred only at high temperatures.

The ir spectrum of the polymer presented characteristic absorption bands at 2900 (*m*), 1720 (*s*), 1450 (*m*), 1375 (*m*), 1220 (*m*), and 1120 cm⁻¹ (*m*).

The nmr spectrum of PMEPL, taken in ODCB at 100°C and at 220 MHz, is presented in Figure 1. The methyl substituent is found at 1.240 ppm and the methyl group of the ethyl substituent forms the expected triplet at 0.898 ppm. These two resonance groups do not seem to contain any information on the stereoregularity of the chain. However, the two methylene groups contain several peaks related to the stereo-regularity of the polymer – the methylene peak of the ethyl substituent is centered at 1.660 ppm while the methylene group of the main chain is centered at 4.245 ppm. The spectrum of PMEPL is in fact very similar to that of PMPPL.²⁵ In both cases, the polymer is semi-crystalline even if an atactic sample is expected: the ammonium salts used as initiator are not known to have a stereoselective character. In both cases, a satisfactory interpretation of the spectrum in terms of tactic sequences has not so far been successfully obtained. The presence of isotactic sequences has been suggested for PMPPL based on

calorimetric measurements.²⁶ But x-ray data seems to be more easily interpreted in terms of syndiotactic sequences.²⁴ C^{13} and H^1 mnr work on model compounds is in progress in order to solve this problem.²⁶

For mechanical properties measurements, films have been prepared on a laboratory press. The samples were first melted at about 125°C and then slowly cooled to room temperature. The stress-strain measurements were done on an Instron tensile machine, table model 1130. The dynamic measurements were recorded using a Rheovibron DDV-II instrument (Toyo Baldwin Inc.) at frequencies of 3, 5, 11, 35 and 110 Hz in a temperature range of 123–373 K.

X-ray measurements were conducted on an X-ray apparatus made of a Philips generator equipped with a Statton-Warhus camera.²⁷ A CuK_{α} target was used. The camera was calibrated with NaCl crystals.

Differential scanning calorimetry (dsc) measurements were made with a Perkin-Elmer DSC-1B apparatus. The instrument was calibrated with gallium and indium at the same heating rate as that used for the polymer.

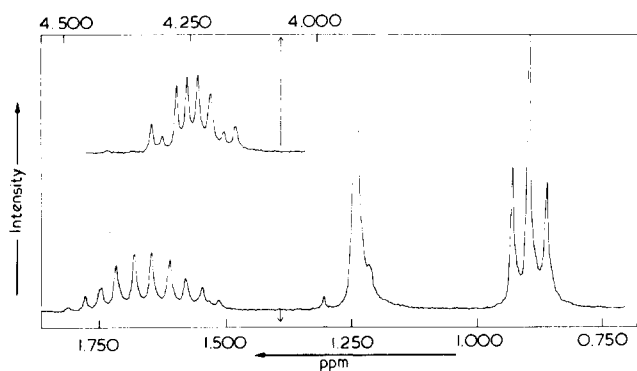


Figure 1 NMR spectrum of PMEPL taken in ODCB at 110°C and 220 MHz

RESULTS AND DISCUSSION

X-ray diffraction

X-ray diffraction was performed first on an undeformed PMEPL sample. The corresponding pattern is shown in Figure 2 and the characteristic lines are listed in Table 1. Upon deformation, the sample necks and the characteristic pattern of the necking region is shown in Figure 2. Its diffraction lines are also shown in Table 1. The diagram of the deformed sample is very similar to the β phase patterns found for P β L, PPL and PMPPL. It is characterized by ± 1 and ± 2 layer lines which are not composed of individual lines but of a continuous streak. From the angular position of these streaks, a c -axis value of 0.475 nm has been

Table 1 X-ray data of PMEPL

Intensity	2θ	d (nm)	Layer line no	
m	8.6	1.03	0	Phase β
s	14.0	0.63	0	
m	16.9	0.52	0	
w	20.4	0.44	0	
m	24.0	0.37	0	Phase α
m	19.6	0.45	1	
w	25.8	0.35	1	
m	40.0	0.22	2	
vs	9.8	0.90	—	Phase α
s	14.9	0.59	—	
vs	16.6	0.53	—	
m	21.3	0.42	—	
w	22.8	0.39	—	Phase α
m	26.6	0.33	—	
w	29.7	0.30	—	
m	33.0	0.27	—	
m	38.2	0.24	—	Phase α
w	42.3	0.21	—	

vs = very strong; s = strong; m = medium; w = weak.

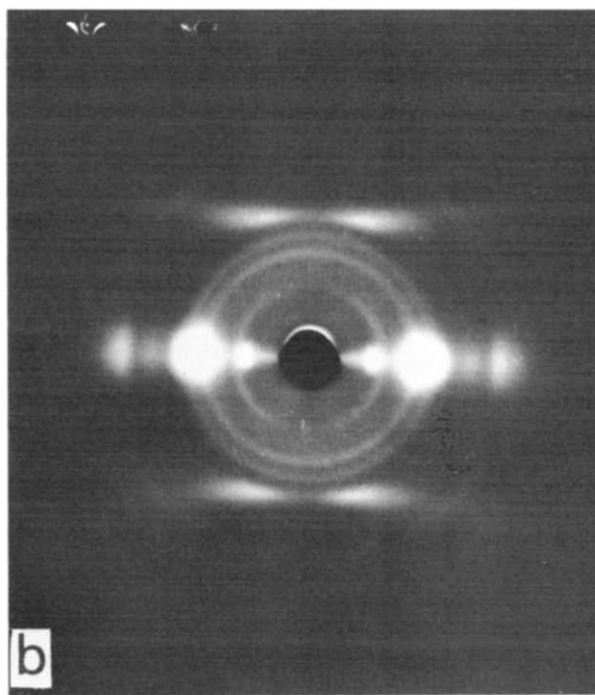
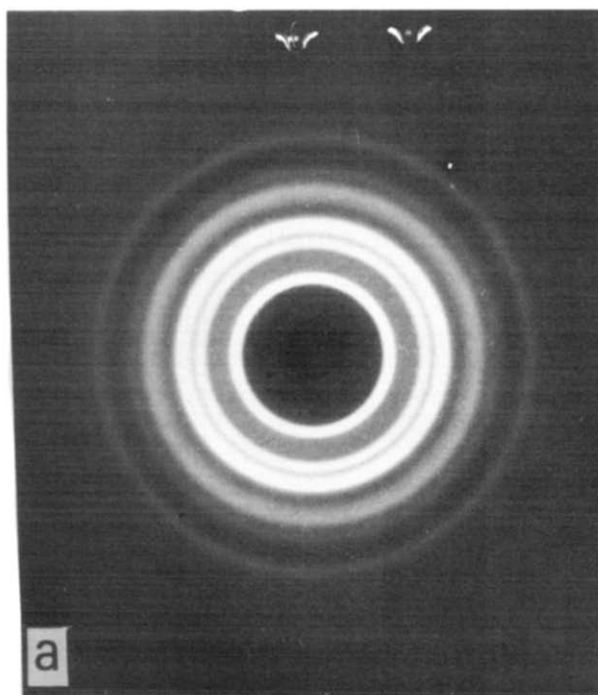


Figure 2 X-ray patterns for undeformed, left, and deformed, right, polymers

calculated for PMEPL which is similar to the values found for P β L, PPL and PMPPL. It corresponds to the length of the repeat unit of PMEPL in an extended planar zig-zag conformation. This result has been explained quantitatively for P β L by Suehiro, Chatani and Tadokoro²² who have shown that the streak was related to a sheet structure parallel to the ac plane, where the mutual levels of the chains along the fibre axis are irregular. The X-ray diagram of PMEPL is certainly due to the same sort of arrangement.

Upon annealing the deformed sample, the α form is recovered and the β crystalline form is completely lost. A reversible crystal-crystal transformation has then been produced which is schematically described in Figure 3. Again, the same sort of transition has been observed for P β L, PMPPL and PPL. However, for PPL, the transition is easily induced in fibres but it can hardly be induced in films. PPL films are brittle and they have elongations at rupture of less than 15% at room temperature. Despite patents that claim that PPL can be stretched to elongations at rupture larger than 100%,^{28,29} we have not succeeded in reproducing these results. But fibres, even those prepared in a very crude way and which do not have a very high degree of initial orientation, can lead to the β crystalline form. Similarly, the β form can hardly be induced in poly (α , α -diethyl- β -propiolactone) (PDEPL) films. PDEPL, even if it has a degree of crystallinity which is much lower than that of PPL, is also a brittle polymer (Table 2) and it cannot be stretched enough to produce the β phase.

Since a β phase is produced upon stretching the PMEPL, the α crystalline phase cannot be obtained for an oriented film and its crystalline structure easily determined. By analogy with the results of P β L, PMPPL and PPL, one expects to have a 2₁ crystalline conformation in PMEPL with a repeat distance of 0.60 nm; but the results presented here do not prove this conclusion. It is interesting to note that it has been necessary to graft a PMPPL chain to an elastomer in order to be able to obtain a satisfactory fibre diagram and to determine its crystalline α structure.²⁴ The situation may be identical for PMEPL.

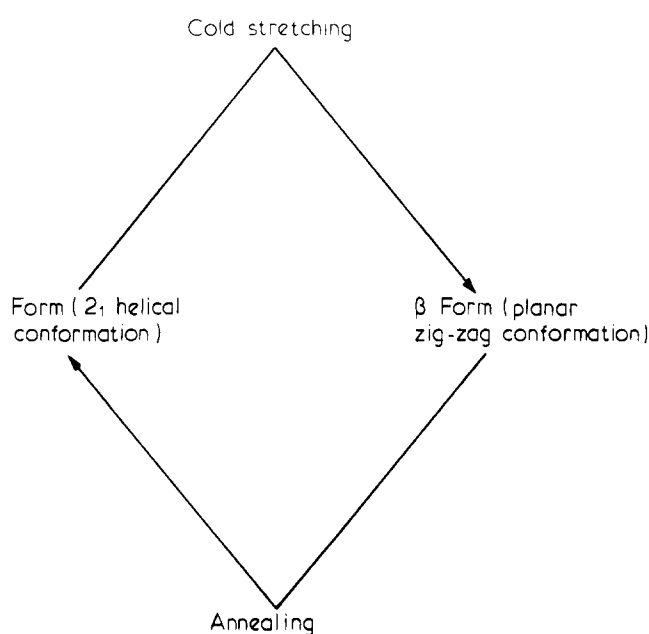


Figure 3 Schematic diagram of the reversible phase transformation in PMEPL

Table 2 Comparative properties of P β L, PMPPL, PMEPL, PEDPL and PPL

	P β L	PMPPL	PMEPL	PDEPL	PPL
Density (gcm ⁻³)	1.38	1.07	1.10	—	1.19
Modulus (MPa)	—	130	247	—	1130
Maximum elongation (%)	—	≈ 750	≈ 30	≈ 15	≈ 10
α - β transition	Yes	Yes	Yes	Not reported yet	Reported on fibres
T_g^b (K)	—	303	290	333	373
T_m^0 (K)	357	370	(393) ^a	531	513
ΔH (Jg ⁻¹)	20	20	27	47	120
ΔH^0 (kJ mol ⁻¹)	8.4	—	—	21	14.8
Degree of crystallinity (%)	≈ 30	—	—	≈ 28	≈ 80
E_a^c (kJ mol ⁻¹)	—	132	200	300	219

^a This value is not a thermodynamic melting point

^b Values obtained by dynamic mechanical measurements at 110 Hz

^c Values obtained by a dynamic experiment

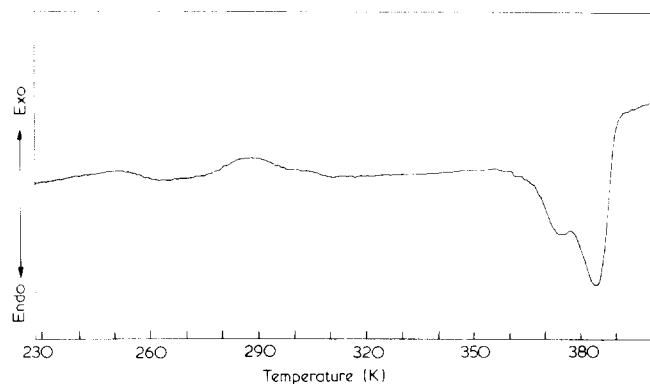


Figure 4 DSC heating curve at 20°C/min

Calorimetry

Calorimetry has been used to determine the glass transition temperature, T_g , the melting temperature, T_m , and the enthalpy of fusion, ΔH , of PMEPL. The calorimetry curve of PMEPL is shown in Figure 4 for a sample prepared by cooling the melt to 225 K. The heating rate was 20 K/min. The curve of Figure 4 is characterized by three different features: a—there is a jump in C_p around 260 K corresponding to T_g ; b—there is an exothermic peak around 285 K indicating most probably an additional crystallization of the sample; c—there is a large endothermic peak around 390 K corresponding to the melting curve of PMEPL. The end of the melting curve at 393 K defines the melting point of the sample. The surface under the melting curve corresponds to an enthalpy of fusion ΔH of 27 Jg⁻¹. These different parameters can be compared to the corresponding values for P β L, PMPPL, PDEPL and PPL (Table 2).

The melting point of PMEPL is not a thermodynamic melting point contrary to other values reported in Table 2. However it is clear that it is intermediate between the value found for PMPPL and those found for PPL and PDEPL. This result confirms the initial measurements of Thiebaut, Fisher, Etienne and Coste.^{30,31} These authors found a melting point of 398 K for PMEPL. They also suggested

that the melting points of the poly (α , α -disubstituted- β -propiolactones) were decreasing with the increase in the size ratio of the two substituents. This conclusion seems to be confirmed by the actual measurements.

The present measurements indicate that in the polylactone series the degree of crystallinity increases in the following order: PMPPL < PMEPL < PDEPL < PPL. This conclusion is reached by comparison of the different ΔH . Of course, the enthalpy of fusion of the pure crystal, ΔH^0 , would be necessary in order to calculate quantitatively the degree of crystallinity of PMEPL and of PMPPL. But the tendency suggested above is in agreement with the dynamic mechanical results presented in the next section of this paper.

It is difficult to explain the low value of T_g of PMEPL. One would expect it to have a value larger than that of PMPPL since the melting point of PMPPL is lower than that of PMEPL and since the propyl substituent of PMPPL should be more mobile and should create more free volume than the ethyl substituent of PMEPL. This anomaly is unexplained but it is confirmed by the dynamic mechanical results presented in the next section of this paper.

Finally, two peaks are found in the melting curve of PMEPL. In the polylactone series, it is usual to have multiple melting peaks. They can be attributed in some instances to different crystal structures¹⁵ and in some other cases to different morphological structures.³² More work is necessary in order to distinguish between these two possibilities in the case of PMEPL.

Dynamic mechanical properties

As shown in Table 2, the stress-strain curve of PMEPL leads to a Young modulus of 247 MPa and to an elongation at rupture of $\approx 30\%$. These two values indicate that PMEPL has a higher degree of crystallinity than PMPPL. The elongation at rupture of PMEPL is closer to those of PPL and PDEPL than to that of PMPPL. Upon deformation, necking occurs at about 10% elongation and the α - β transition is produced at the necking point, as in the case of PMPPL.

The Rheovibron measurements at 110 Hz lead to the storage moduli, E' , to the loss moduli, E'' and to the phase angles δ which are shown in Figures 5 and 6 as a function of temperature. The experimental values of $\tan \delta$ were corrected according to Massa's equation.^{33,34} The maximum in $\tan \delta$ is seen at 290 K and it has an intensity of 0.202. This peak is clearly the T_g of PMEPL. It is found at a higher temperature than the value obtained in calorimetry because the Rheovibron measurements were done at high frequencies. It has a lower intensity than the corresponding peak of PMPPL, 0.450,³⁵ but it is larger than the PDEPL β peak, 0.185,³⁶ indicating an intermediate degree of crystallinity.

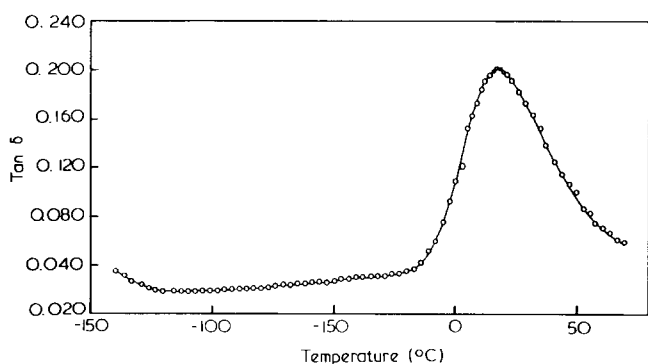


Figure 5 $\tan \delta$ — temperature dependence of PMEPL at 110 Hz

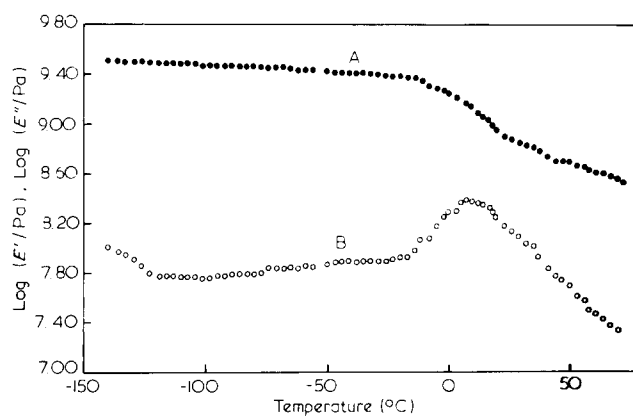


Figure 6 E' and E'' — temperature dependence of PMEPL at 110 Hz. A, $\log E'$; B, $\log E''$

The maximum in T_g at 290 K for the $\tan \delta$ curve is associated with an absorption peak in the E'' curve and to a dispersion curve of E' .

At low temperatures, an increase in $\tan \delta$ and in E'' is observed, suggesting the presence of a secondary relaxation peak around 120 K. This relaxation process must be associated with the amorphous fraction of the polymer because of the low degree of crystallinity of PMEPL. It is suggested that it is due to the motion of the ethyl substituent of PMEPL since this peak has been observed previously for polylactones having an ethyl or propyl substituent (PMPPL, PDEPL) but not for that having a methyl substituent (PPL).^{35,36} For the latter sample, the methyl relaxation mechanism must occur in a temperature range which is not covered in the Rheovibron experiment.

For the β relaxation process, an apparent activation energy, E_a , can be calculated using Arrhenius' equation:

$$F = F_0 \exp [-E_a/RT] \quad (1)$$

where F is the measuring frequency, F_0 is the frequency when T approaches infinity, and T is the temperature corresponding to a maximum in the $\tan \delta$ curve at the measuring frequency F . The least squares method applied to the results yielded an apparent activation energy of 200 kJ mol⁻¹. This value is of the same order of magnitude as those found for other polylactones (Table 2).

CONCLUSIONS

A polylactone of the poly (α , α -disubstituted- β -propiolactone) series has been prepared and it has been shown to present a reversible α - β transition. The α helical form is obtained under usual crystallization conditions; the β planar zig-zag form is obtained upon stretching and the α form is re-obtained by annealing. The β form has a sheet structure with its chains being irregularly arranged along the fibre axis.

PMEPL has a T_g of 260 K and a melting point of 393 K. Its low value of enthalpy of fusion, 27 kJ g⁻¹, indicates a low degree of crystallinity.

The low T_g of PMEPL is also found by dynamic mechanical experiments, where at 110 Hz, a T_g of 290 K is observed along with a $\tan \delta$ peak of high intensity characteristic of a sample of low degree of crystallinity. A second increase in intensity of the $\tan \delta$ curve is observed at low temperatures suggesting the presence of a secondary relaxation process around 120 K.

ACKNOWLEDGEMENTS

The authors thank Ms Madeleine Aubin for the thermal measurements and Mr Joseph Noah for the dynamic mechanical measurements. They also thank the National Research Council of Canada and the Ministry of Education of the Province of Québec (FCAC program) for the research grants that supported this work.

REFERENCES

- 1 Mayne, N.R. *Chemtech* December 1972, 728, Mayne, N.R. *Advances in Chemistry Series* (Eds N.A. Platzer) (1973), **129** p 175
- 2 Oosterhof, H.A. *Polymer* **15**, 49
- 3 Sundet, S.A., Thamm, R.C., Meyer, J.M., Buck, W.H., Caywood, S.W., Subramanian, P.M. and Anderson, B.C. *Macromolecules* **9**, 373
- 4 Foss, R.P., Jacobson, H.W., Cripps, H.N. and Sharkey, W.H. *Macromolecules* **9**, 373
- 5 Buck, W.H. *Rubber Chem Tech* 1977, **50**, 109
- 6 Caywood, S.W. *Rubber Chem Tech* 1977, **50**, 127
- 7 Sundet, S.A. *Macromolecules* 1978, **11**, 146
- 8 Thamm, R.C. and Buck, W.H. *J Polymer Sci, Polymer Chem Ed* 1978, **16**, 539
- 9 Sharkey, W.H., Foss, R.P. and Harris, J.F. 'Polymer Alloys', (Eds D. Klemperer and K.C. Frisch), Plenum Press, NY, 1977, pp 159-174
- 10 Sundet, S.A. and Thamm, R.C. 'Polymer Alloys', (Eds D. Klemperer and K.C. Frisch), Plenum Press, NY, 1977, pp 175-189
- 11 Buck, W.H. 'Polymer Alloys', (Eds D. Klemperer and K.C. Frisch), Plenum Press, NY, pp 191-204
- 12 Allegrezza, A.E. PhD Thesis, University of Massachusetts, Amherst, 1972
- 13 Allegrezza, A.E., Lenz, R.W., Cornibert, J. and Marchessault, R.H. *J Polymer Sci, Polymer Chem Ed* **16**, 2617
- 14 Lenz, R.W., Dror, M., Jorgensen, R. and Marchessault, R.H. *Polymer Eng Science* 1978, **18**, 937
- 15 Prud'homme, R.E. and Marchessault, R.H. *Makrom Chemie* 1974, **175**, 2705
- 16 Prud'homme, R.E. and Marchessault, R.H. *Macromolecules* 1974, **7**, 541
- 17 Knoblock, F.W. and Statton, W.O. *US Patent 3 299 171*, 1967
- 18 Carazzolo, G. *Chim Ind (Milan)*, 1964, **46**, 525
- 19 Cornibert, J., Hien, N.V., Brisse, F. and Marchessault, R.H. *J Can Chimie* 1974, **52**, 3742
- 20 Wasai, K., Saegusa, T. and Furukawa, J. *Kogyo Kagaku Zasshi* 1964, **67**, 601
- 21 Kagiya, T., Sano, T. and Fukui, K. *Kogyo Kagaku Zasshi* 1964, **67**, 451
- 22 Suehiro, K., Chatani, Y. and Takokoro, H. *Polymer J* 1975, **7**, 352
- 23 Cornibert, J., Marchessault, R.H., Allegrezza, A.E. and Lenz, R.W. *Macromolecules* 1973, **6**, 676
- 24 Marchessault, R.H., St-Pierre, J., Duval, M. and Perez, S. *Macromolecules*, in press
- 25 Prud'homme, R.E., Leborgne, A. and Spassky, N. unpublished results
- 26 Spassky, N., Leborgne, A., Reix, M., Prud'homme, R.E., Bigdeli, E. and Lenz, R.W. *Macromolecules* 1978, **11**, 716
- 27 Alexander, A.L. 'X-ray Diffraction Methods in Polymer Science', Wiley, NY, 1969
- 28 Brit Patent 1 066 123, 1967
- 29 Kitazawa, T. and Onga, M. Fr Patent 1 569 683, 1969
- 30 Thiebaut, R., Fischer, N., Etienne, Y. and Coste, J. *Ind Plastiques Modernes*, 2 March 1962, **1**
- 31 Etienne, Y. and Fischer, N. *Fr Patent 1 231 163*, 1960
- 32 Normand, Y., Aubin, M. and Prud'homme, R.E. *Die Makrom Chemie*, 1979, in press
- 33 Massa, D.J. *J Appl Phys* 1973, **44**, 2595
- 34 Ramos, A.R., Bates, F.S. and Cohen, R.E. *J Polymer Sci, Polymer Physics Ed* 1978, **16**, 753
- 35 Noah, J. and Prud'homme, R.E. submitted to *Macromolecules*
- 36 Noah, J. and Prud'homme, R.E. submitted to *Die Macromolekulare Chemie*