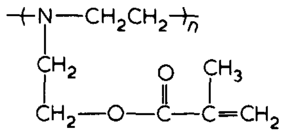
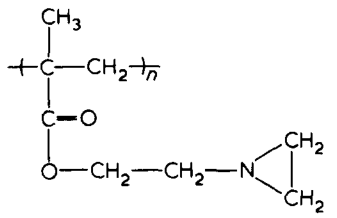
From these results it can be concluded that anodic polymerization of AEMA occurs through the aziridinyl group to yield a polymer of the structure:



The cathodic polymerization takes place by the opening of the double bond to give a polymer of the following structure:



Selective polymerization through either of the two functional groups of AEMA can thus be achieved by electroinitiation.

ACKNOWLEDGEMENT

We are indebted to Dr K. N. Somasekharan for helpful discussions. This research was supported by a grant from the Office of Naval Research.

REFERENCES

1 Funt, B. L. and Tanner, J. *Tach. Chem.* (N.Y.), 1975, **5(2)**, 559
2 Subramanian, R. V. *Adv. Polym. Sci.* 1979, **33**, (in press)
3 Subramanian, R. V. and Jakubowski, J. J. *Polym. Eng. Sci.* 1978, **18**, 590
4 Subramanian, R. V., Patel, A. K. and Sundaram, V. *Proc. SPI Reinf. Plast. Comp. Inst.* 1978, 20F
5 Subramanian, R. V., Jakubowski, J. J. and Williams, F. D. *J. Adhesion*, 1978, 9, 185
6 Subramanian, R. V., Jakubowski, J. J. and Garg, B. K. *Polym. Prepr.* 1978, **19** (1), 517
7 Subramanian, R. V. and Garg, B. K. *Polym. Bull.* 1979, **1**, 421
8 Dermer, O. C., Ham, G. E. 'Ethyleneimine and Other Aziridines', Academic Press, New York, 1969
9 Jones, G. D. in 'The Chemistry of Cationic Polymerizations', P. H. Plesch, Ed., MacMillan, New York, 1963, Ch 14

Preparation and characterization of spin-labelled polystyrene

C. Friedrich and C. Noël
Laboratoire de Physicochimie Structurale et Macromoléculaire, ESPCI, 10, rue Vauquelin, 75231 Paris Cédex 05, France
and R. Ramasseul and A. Rassat
Laboratoire de Chimie Organique et Physique, Centre d'Etudes Nucléaires de Grenoble, 85x, F38041 Grenoble, France
(Received 23 July 1979; revised 22 October 1979)

The dynamic properties of polystyrene in dilute solutions constitute a problem of considerable interest. In recent years, many investigations have been carried out using techniques well-adapted to the study of fast movements such as fluorescence polarization[1], ^{13}C and ^{1}H nuclear magnetic relaxation[2–7], ultrasonic relaxation[8–11] and Raman line shape analysis[12] to find a description of the molecular motions under a variety of conditions. The spin labelling technique has recently been used to study polystyrenes labelled either at chain ends[13] or at the *para*-[14] or at the *meta*-[15] position of the aromatic ring. The present work is concerned with the preparation and characterization of a polystyrene with a nitroxide group inserted in the main chain.

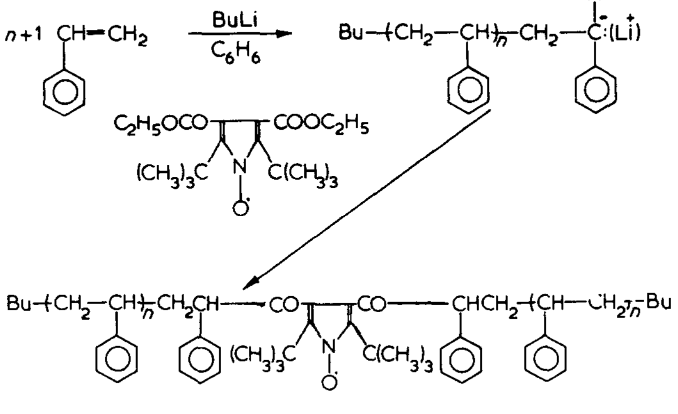
Basically, the method consists of adding a bifunctional deactivating reagent to the monofunctional 'living' polymer prepared by anionic polymerization, using butyllithium as the initiator and 2,5-di-*t*-butyl-3,4- diethoxycarbonyl pyrrol-2-yloxy as the deactivating agent (shown in the reaction scheme).

Benzene was dried over calcium chloride and freed from moisture by refluxing over sodium wire. It was then twice distilled over sodium wire and stored over sodium.

Styrene was three times distilled over sodium wire under reduced pressure.

Butyllithium in benzene was freshly prepared before each polymerization by reaction of butyl chloride and lithium metal.

2,5-di-*t*-butyl-3,4- diethoxycarbonyl pyrrol-1-yloxy was prepared as described in ref 16.



0032–3861/80/020232–04\$02.00

Benzene (85 ml) was distilled into the reaction vessel from its reservoir. Butyllithium and styrene (9 g) were added drop by drop under argon at room temperature. The resultant orange coloured solution was stirred. After the required reaction time (2–3 h) a small part of the solution was isolated in a side arm of the reaction vessel and precipitated in heptane. Simultaneously, a slight excess of 2,5-di-*t*-butyl-3,4- diethoxycarbonyl pyrrol-1-yloxy in benzene was introduced gradually by syringe through a serum cap into the vigorously stirred 'living' polymer solution. The contents turned green. Progressively, the colour disappeared and the viscosity of the solution increased. The contents were stirred for 1 h to ensure that all the deactivating agent had reacted. The reaction product was precipitated in heptane. The spin-labelled polymer was purified by repeated precipitation in heptane from benzene solution in order to remove the unreacted deactivating agent. The purification was carried out until the correlation time of a standard polymer solution fell to a constant value. The resultant spin-labelled polystyrene was characterized by a molecular weight of 62 800 and a polydispersity of 1.10 as determined by gel permeation chromatography using universal calibration.

The X-band e.s.r. measurements were performed on a Varian E_4 spectrometer. The sample solutions were prepared in standard e.s.r. tubes at a fixed composition of 10% by wt. Each solution was subjected to at least four freeze–pump–thaw cycles and sealed off under dynamic vacuum. Temperature was controlled to ±0.5K. Field measurements were made with a Direct Reading Frequency Meter (Radiall) and isotropic g values were measured by comparison with the spectrum of 1,1-diphenyl-2- picrylhydrazyl for which $g = 2.0036$.

For illustrative purposes, we give some e.s.r. spectra of the spin-labelled polystyrene in toluene solution in *Figure 1*. Two discrete processes are evident above and below a transition zone covering the temperature range 40°–75°C. At high temperature in particular the isotropic nitrogen coupling constant a^N_{iso} is slightly smaller and the isotropic g-factor g_{iso} is slightly larger than at low temperature. The interplay of these A- and g- value shifts causes the spectra to overlap asymmetrically so that at 9.5 GHz only the high field lines are resolved. The sub-splitting which is found at this high-field peak of the triplet above 30°C and below 80°C indicates that the labels are in two different surroundings, suggesting that a certain transition has occurred in the sample. This temperature range effectively corresponds to the 'phase transition' evidenced by several authors using different experimental techniques as reviewed in ref 17.

At 90°C, the e.s.r. spectrum is not a composite one so that, as for earlier studies of dilute polymer solutions[13–15,18], the line widths can be analysed according to the expression:

$$T_{2(m_I)}^{-1} = A + Bm_I + Cm_I^2$$

where, omitting nonsecular contributions with:

$$B = -\left(\frac{4}{15}\right) b\Delta_\gamma B_0 \tau_c$$

and

$$C = \left(\frac{b^2}{8}\right) \tau_c$$

B_0 is the applied magnetic field and τ_c the rotational correlation time. The determination of the parameters

$$b = \frac{4\pi}{3}\left(T_{ZZ} - \frac{1}{2}(T_{XX} + T_{YY})\right)$$

and

$$\Delta_\gamma = \frac{-|\beta|}{\hbar}\left\{g_{ZZ} - \frac{1}{2}(g_{XX} + g_{YY})\right\}$$

involves a knowledge of the isotropic nitrogen coupling constant a^N_{iso}, the isotropic g-factor g_{iso} and components of the anisotropic g and hyperfine coupling tensors. The isotropic parameters were determined from the spectrum of the label in toluene. At 20°C, the measured values of a^N_{iso} and g_{iso} were 4.60 and 2.0062, respectively, which compare favourably with the values of 4.58 and 2.0061 obtained by Rassat *et al.*[19] for the label in benzene solution. It is possible

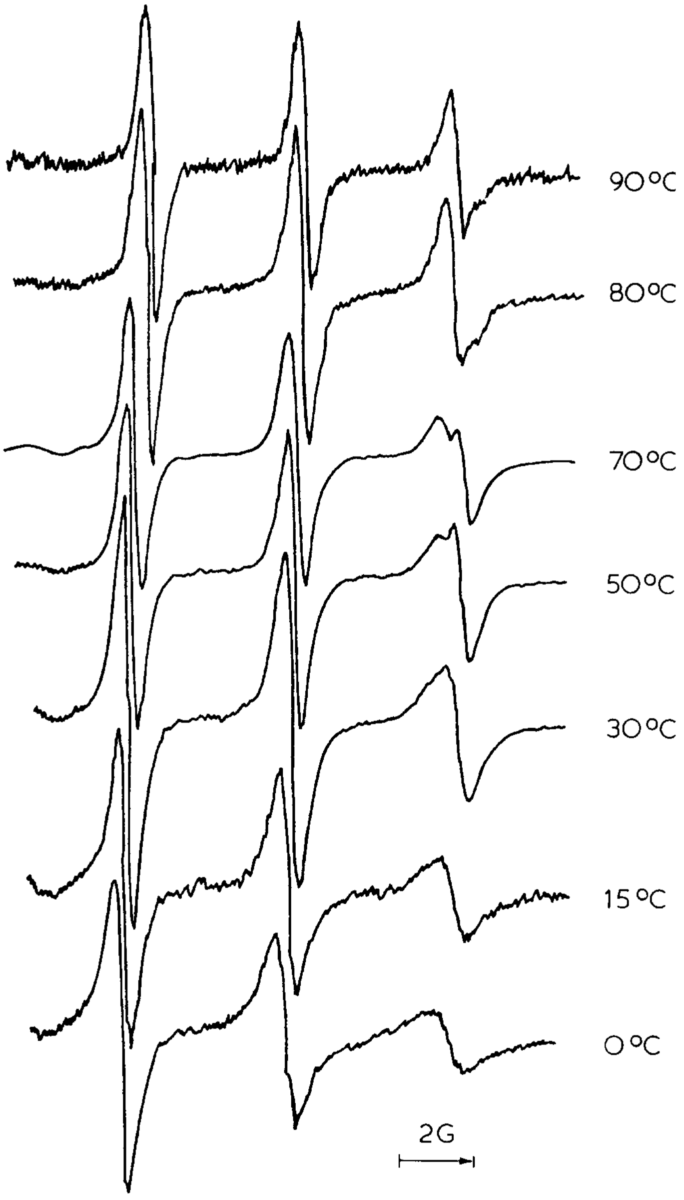


Figure 1 The temperature dependence of the e.s.r. spectra of spin-labelled polystyrene in toluene solution

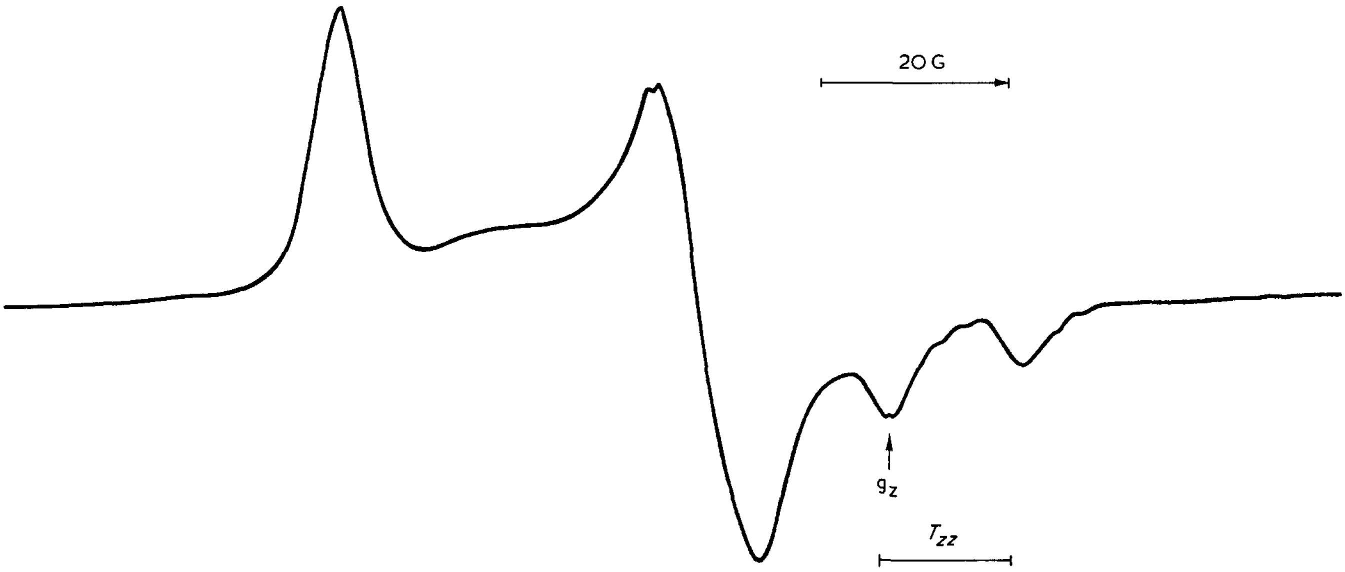


Figure 2 35 GHz rigid spectrum for 2,5-di-*t*-butyl-3,4-diethoxycarbonyl pyrrol-1-yloxy in a toluene glass as 143K

accurately to determine T_{ZZ} and g_{ZZ} from the 35 GH$_Z$ rigid spectrum of the label in toluene at 143K (*Figure 2*). T_{ZZ}: 14 G is equal to one half the separation between the outer hyperfine extrema while g_{ZZ}: 2.00206 corresponds to the mid-point of these two extrema. Combining the value of a^{N}_{iso} with that of T_{ZZ} and making the assumption of axial symmetry in the hyperfine interaction tensor leads to $T_{XX} = T_{YY} \simeq 0$. Since

$$g_{iso} = \frac{1}{3}\left(g_{XX} + g_{YY} + g_{ZZ}\right)$$

then

$$g_{XX} = g_{YY} = 2.00827.$$

Defining the ratios $T_{2(0)}/T_{2(+1)}$, $T_{2(0)}/T_{2(-1)}$ as R_+ and R_-, respectively, it is readily shown that:

$$R_+ + R_- - 2 = 2CT_{2(0)} = \frac{b^2}{4} T_{2(0)}\tau_{c_C} \qquad (1)$$

$$R_+ - R_- = 2BT_{2(0)} = -\left(\frac{8}{15}\right) b\Delta_\gamma B_0 T_{2(0)}\tau_{c_B} \qquad (2)$$

If the individual lines are expected to be Lorentzian in shape, then $T^{-1}_{2(0)} = \pi(3)^{1/2}\Delta\nu$ where $\Delta\nu$ is the peak-to-peak width of the central hyperfine component. R_+ and R_- are given by:

$$R_\pm = \left[\frac{Y_{(0)}}{Y_{(\pm 1)}}\right]^{1/2}$$

in which the Y values are peak-to-peak intensities. The spectral simulation technique allows one to correct $T_{2(0)}$ and $R_\pm$ for inhomogeneous broadening due to unresolved proton coupling.

The values of $\tau_{c_B} = 1.5_1 \times 10^{-10}$ s and $\tau_{c_C} = 2.0_6 \times 10^{-10}$s thus calculated from the B and C coefficients in (1) and (2) are almost coincident if due allowance for experimental errors is made. Such a result indicates that the inserted group rotation is essentially isotropic in accordance with the tumbling rate of the chain ends[13] and the side chains[14] of polystyrene which was found isotropic.

The mean correlation time obtained at 90°C for the in-chain labelled polystyrene is much longer than that of end-labelled polystyrene [8×10^{-11} s] [13,20] but in satisfactory agreement with that of side-chain labelled polystyrene [$1.4_9 \times 10^{-10}$ s] (ref 14). It lends further support to earlier statements[15,20] that (i) a spin label at the chain end experiences less steric hindrance against rotation and is less strongly coupled to the motion of neighbouring bonds than a spin label inserted in the main chain (ii) segmental reorientation is the main factor controlling τ_c in side-chain labelled polystyrene of high molecular weight.

A meaningful estimate of the correlation times, under the whole temperature range, requires a more accurate determination of T_{XX}, T_{YY}, g_{XX} and g_{YY} and an analysis of the e.s.r. line shapes by summing two spectral components, and varying the proportions of the two components at each temperature. The results of e.s.r. studies relative to the dependence of the correlation times thus obtained on temperature, solvent nature and viscosity will be published in detail in due course.

References

1 Valeur, B. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 11

2 Laupretre, F., Noël, C. and Monnerie, L. *J. Polym. Sci. Polym. Phys. Edn.* 1977, **15**, 2127

3 Allerhand, A. and Hailstone, R. K. *J. Chem. Phys.* 1972, **56**, 3718

4 Schaefer, J. and Natusch, D. F. S. *Macromolecules* 1972, **5**, 416

5 Heatley, F. and Begum, A. *Polymer* 1976, **17**, 399; Heatley, F. and Wood, B. *Polymer* 1978, **19**, 1405

6 Gronski, W. and Murayama, N. *Makromol. Chem.* 1978, **179**, 1509, 1521

7 Inoue, Y., Konno, T. *Polym. J. Jpn.* 1976, **8**, 457

8 Froelich, B., Noël, C., Monnerie, L. *Polymer* 1979, **20**, 529

9 Nomura, H., Kato, S., Miyahara, Y. *Mem. Fac. Eng., Nagoya Univ.* 1975, **27**, 72

10 Lemarechal, P. *Thèse de Doctorat d'Etat*, Strasbourg, 1971

11 Cochran, M. A., Dunbar, J. H., North, A. M. and Pethrick, R. A. *J. Chem. Soc., Faraday Trans.* II, 1974, **70**, 215
12 Koda, S., Nomura, H. and Miyahara, Y. *Macromolecules* 1978, **11**, 604
13 Bullock, A., Cameron, G. G. and Reddy, N. K. *J. Chem. Soc., Faraday Trans.* I, 1978, **74**, 727
14 Bullock, A., Cameron, G. G. and Smith, P. M. *J. Chem. Soc., Faraday Trans.* II, 1974, **70**, 1202
15 Bullock, A., Cameron, G. G. and Smith, P. M. *Polymer* 1973, **14**, 525
16 Ramasseul, R. and Rassat, A. *Bull. Soc. Chim.* 1970, 4330
17 Nguyen-Luong Bach Van, Noël, C. and Monnerie, L. *J. Polym. Sci. Polym. Symp.* 1975, **52**, 283
18 Lang, M. C., Laupretre, F., Noël, C. and Monnerie, L. *J. Chem. Soc., Faraday Trans.* II, 1979, **75**, 349
19 Grossi, P. J., Marchetti, L., Ramasseul, R. and Rassat, A. *J. Chim. Phys.* 1977, **74**, 1167
20 Yang, H. W. H. and Chien, J. C. W. *Macromolecules* 1978, **11**, 759

Characterization of deformation phenomena in polymers by rapid-scanning Fourier transform infra-red (FT i.r.) spectroscopy and mechanical measurements: 1. Orientation of isotactic polypropylene during uniaxial deformation

G. Bayer and W. Hoffmann
Bayer AG, Werk Leverkusen, D 5090 Leverkusen, West Germany
H. W. Siesler
Bayer AG, Werk Dormagen, D 4047 Dormagen, West Germany

(Received 13 November 1978; revised 20 June 1979)

INTRODUCTION

In recent years there has been steadily increasing interest in the effects of mechanical stress on the vibrational spectra of polymers and in the determination of spectroscopic orientation parameters which may provide some insight into the deformation mechanism. I.r. dichroism measurements of polymers under mechanical load reported previously[1–7] have been restricted to the application of conventional dispersive instrumentation. Owing to the long scan duration of dispersive instruments, the characterization of orientation in deformation processes has been limited so far to stepwise procedures. The orientation values derived from the i.r. dichroism of particular absorption bands then refer to the sample at the relaxed stress levels of the individual elongation steps which commonly differ signfiicantly from the corresponding unrelaxed stress levels of a continuously measured stress–strain curve. Thus, it has been demonstrated by rapid-scan X-ray diffraction that different changes in crystal orientation can be observed during stress relaxation of polyethylene dependent on the strain level under examination[8]. In so-called dynamic i.r. (d.i.r.) investigations of polypropylene, Wool and Statton[2–5] have detected changes in orientation during stress relaxation as a function of time by continuously monitoring the intensity of polarized absorption bands at constant wavenumber with dispersive instrumentation. However, this technique is not generally applicable – apart from the fact that it requires multiple experiments for various absorption bands – because the frequency shifts observed for stress-sensitive absorption bands[1,3,5] would severely bias the results of such investigations. Furthermore, it has been pointed out[2,3,5] that samples tested at the same strain level can have widely varying molecular mechanics as a function of strain history. Hence, strictly speaking, the structural conclusions derived on a microscopic scale from spectroscopic orientation measurements in stepwise elongation procedures should not be correlated with the macroscopic deformation properties reflected by continuously measured stress–strain diagrams. However, this situation has been largely improved by the introduction of rapid-scanning *FT* i.r. spectrometers. With such systems, intensity changes, dichroic properties, band shapes and frequency shifts of absorption bands can be monitored simultaneously with the deformation process over the entire mid-infrared region in very small strain intervals relative to the total elongation. Additionally, the influence of stress relaxation on particular absorption bands may be tested in the fast and slow decay region during short time intervals.

The effect of orientation on a particular absorption band in the i.r. spectrum of a polymer is generally expressed by the dichroic ratio R:

$$R = \frac{A_{\parallel}}{A_{\perp}} \qquad (1)$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances measured with radiation polarized parallel and perpendicular to the draw direction, respectively.

In order to characterize the chain alignment of a uniaxially oriented polymer, it is convenient to define an orientation function[9,10] f:

$$f = \frac{(3\langle\cos^2\Theta\rangle - 1)}{2} \qquad (2)$$

with Θ representing the angle between the stretching direction and the axis of the chain segments. This function f has a value of unity for a sample whose polymer chains are completely oriented in the stretch direction. For perfect trans-

0032–3861/80/020235–04$02.00