Polymerization and dipole moment of poly(allyl cyanide)

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Polymerization of allyl cyanide was carried out by radiation and chemical catalysis. Polymers obtained by γ-rays under various conditions such as in bulk and in the presence of either air or 0.1 mol% $ZnCl_2$ were oily or solid dark-brown products with molecular weights up to 1.4×10^4. The polymers obtained by n-BuLi was a pale-yellow solid, insoluble in common organic solvents and water. No polymer was obtained with $BF_3O(C_2H_5)_2$. The mechanism of polymerization was shown by infra-red investigation to be different for radiation and catalyst polymerization. The relation between intrinsic viscosity and number-average molecular weight was found to be $[\eta] = 4.4 \times 10^{-4} M_n^{0.51}$. The dipole moment ratio D_∞ of poly(allyl cyanide) in 1,4-dioxane was measured. The relatively large value of D_∞ shows that the polymer chain is not very rigid. A conformational change was observed at 40°C based on dipole moment measurements.

(Keywords: radiation polymerization; intrinsic viscosity; dipole moment; chemical catalyst; conformational transition; allyl cyanide; oily polymer; γ-rays)

INTRODUCTION

Monoallyl compounds, $CH_2{=}CH{-}CH_2{-}X$ do not polymerize readily by radiation to give high-molecular-weight polymers. Their reactivity depends on the substituent group X. It was shown that, when X was urea[1] or thiourea[2], monomer could be polymerized easily to give polymers with molecular weights of about 1×10^6. However, when X was –OH or $-NH_2$, bulk polymerization gives low conversion of oligomers, and both conversion and molecular weights increased when the monomer contained additives such as $CaCl_2$, $MgCl_2$, HCl, H_3PO_4, etc.[3,4]. The additives most probably complex with X and decrease the degradation chain transfer of the monomer.

Radiation-initiated polymerization of allyl cyanide has not been reported before. Nakayama *et al.*[15] reported the polymerization with n-BuLi under vacuum at −78°C, which gave 10% conversion in 2 h. The molecular weight was only 730. Conversion decreased with increase of temperature, and no polymer was obtained at 40°C. They showed by i.r. spectroscopy that the repeat unit in polymer chains was $-(CH_3)CH{-}CH(CN)-$.

The electric dipole moment of poly(allyl cyanide) has not been reported before, but that of the monomer has been studied by Cumper *et al.*[6].

In this work, allyl cyanide was polymerized by radiation and chemical catalysis to investigate the kinetics and mechanism of polymerization. The conformational behaviour of the polymer in solution was studied by electric dipole moment measurements. Since all polymers have important industrial applications, their preparation by direct polymerization methods is important.

EXPERIMENTAL

Allyl cyanide (Aldrich) was purified by distillation (b.p. 37°C). Dimethylformamide (DMF; Aldrich) was first distilled over $CuSO_4$ and then redistilled. Dichloromethane and 1,4-dioxane (Merck) were reagent quality and were used without further purification. $BF_3O(C_2H_5)_2$ and n-BuLi (Aldrich) were in hexane solution and used as received.

About 2 ml of pure monomer or monomer containing $ZnCl_2$ were placed in a Pyrex tube and evacuated at 10^{-4}–10^{-5} mmHg for 67 h. The tubes were then sealed and placed in a ^{60}Co γ source at a constant dose rate of 0.100 Mrad h^{-1} for the desired time at a constant temperature. After irradiation the tubes were broken and monomer removed by freeze-drying. The percentage conversion was calculated gravimetrically. For polymerization in air, the samples were irradiated without evacuation of sample tubes. Viscosities of polymer samples were measured in CH_2Cl_2 at 25°C. Molecular weights of several samples were also determined cryoscopically in DMF using as a standard a polystyrene sample with a number-average molecular weight of 4800 and a heterogeneity index of 1.10.

Polymerization by $BF_3O(C_2H_5)_2$ and n-BuLi in hexane was carried out at −14, 25 and 45°C for catalyst concentrations ranging from 0.006 to 0.030 M and monomer concentration of 1.400 M. The reaction time was 50 h. Polymerization was also repeated at fixed concentration of monomer and catalyst for different reaction times. No polymer was obtained with $BF_3O(C_2H_5)_2$. The polymer obtained by n-BuLi was separated by filtration and dried under vacuum to constant weight. The conversion was calculated gravimetrically.

The i.r. spectra of monomer were taken in NaCl cells and those of polymer from KBr pellets.

The 80 MHz ^1H n.m.r. and decoupled 20.13 MHz ^{13}C

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n.m.r. spectra of monomer and polymer were taken in DMSO-d_6 using a Fourier-transform Bruker AC spectrometer. The monomer spectra were also taken in CD_3Cl.

The radiation-induced polymer was soluble only in 1,4-dioxane as a non-polar solvent. Therefore, capacitance measurements were done in 1,4-dioxane with polymer concentrations of about 0.2–0.4 g dl^{-1} in the temperature range 20–50°C using a General Radio Co. type 1620A capacitance-measuring assembly at a frequency of 10 kHz. The temperature of measurements was maintained within an error of ± 0.05°C. The refractive index increments (dn/dc) were measured by a Brice-Phoenix differential refractometer at a wavelength of 436 nm.

RESULTS AND DISCUSSION

Polymerization of allyl cyanide

Allyl cyanide was polymerized in bulk form under vacuum and in air at room temperature. The conversion as a function of irradiation time is plotted in *Figure 1*. The rate of polymerization was very low and required a long irradiation time. However, the irradiation may be shortened by using high dose rates. The change of conversion with time is almost linear for the samples with or without the presence of air. Therefore, the presence of oxygen does not have any effect on polymerization rate.

The conversion–time relation for radiation polymerization of allyl cyanide containing 0.1 mol% $ZnCl_2$ at room temperature is given in *Figure 2*. The kinetic curve is the same as that of the bulk sample. The presence of $ZnCl_2$ in the monomer does not affect the polymerization rate of allyl cyanide, as reported for allyl alcohol[3] or allylamine[4]. This is most probably due to the formation of different complexes of metal halides with allyl cyanide from that of allyl alcohol or allylamine. However, when the concentration of $ZnCl_2$ in the monomer is varied, no polymer could be obtained for $ZnCl_2$ concentrations exceeding 0.2 mol%. At lower concentrations of $ZnCl_2$, conversions were independent of concentrations.

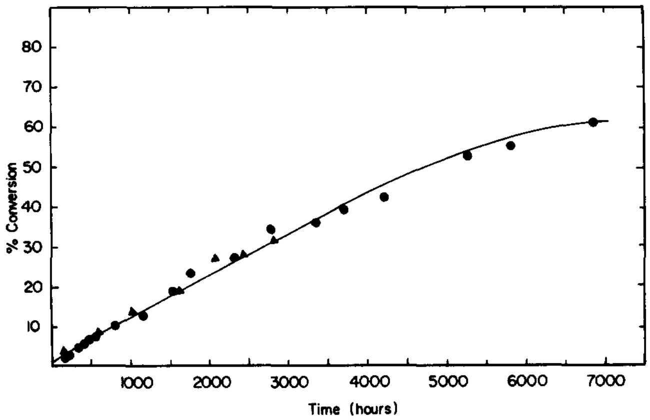


Figure 1 Polymerization of allyl cyanide by radiation: (●) in vacuum; (▲) in air

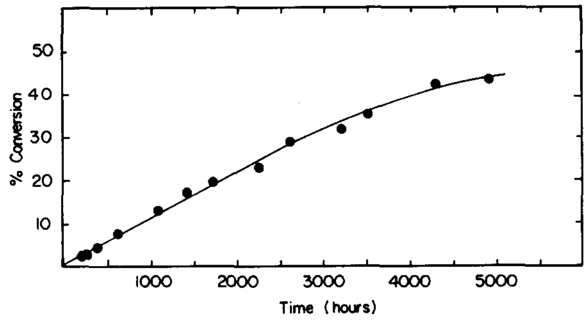


Figure 2 Polymerization of allyl cyanide containing 0.1 mol% $ZnCl_2$ by radiation

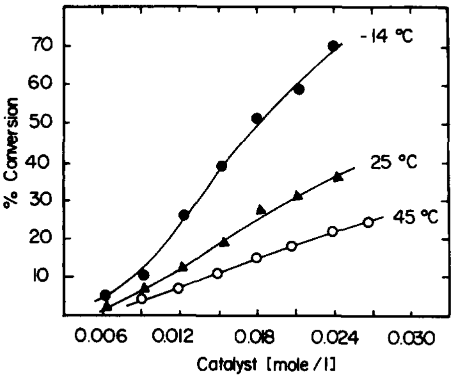


Figure 3 Polymerization of allyl cyanide by n-BuLi

Polymerization of allyl cyanide with $BF_3O(C_2H_5)_2$ was carried out at -14, 25 and 45°C in vacuum conditions, under a nitrogen atmosphere and in air. No polymers were obtained under any of these conditions. However, under similar conditions with n-BuLi a pale-yellow solid polymer was obtained. The polymer was insoluble in common organic solvents and water. The conversion–catalyst concentrations are plotted in *Figure 3* for polymerization at -14, 25 and 45°C. No difference in polymerization rates was observed whether or not vacuum conditions were used. The polymerization rate, however, increased with decrease of temperature. The activation energy calculated from conversion–time kinetic curves was -45.4 kJ mol^{-1}. Our results are different from that of Nakayama *et al.*[5], who have reported no polymer formation at 40°C and very low molecular weights at -78°C. This is most probably because they used a lower concentration of catalyst and shorter reaction time. In the 2 h of reaction time that they reported, we also received very low conversion. The conversion reaches its maximum value in about 40–50 h.

Molecular weights of polymers

Molecular weights of polymers were measured from their viscosities in CH_2Cl_2 at 25°C. The molecular weights of several samples were also measured cryoscopically using DMF as a solvent. The plot of log[η] against log M_n is given in *Figure 4*. From the intercept and slope of the straight line obtained, the relation between the intrinsic viscosity, measured in CH_2Cl_2 at 25°C, and the number-average molecular weight (in the range of 1.3×10^3 to 1.4×10^4) was found to be:

$$[\eta] = 4.4 \times 10^{-4} M_n^{0.51}$$

The number-average molecular weights of polymers obtained by radiation for bulk and $ZnCl_2$-containing monomers are plotted against conversion in *Figure 5*. In both curves the molecular weight increased with conversion, reaching a maximum at about 20% and then decreasing again. The maximum molecular weight in

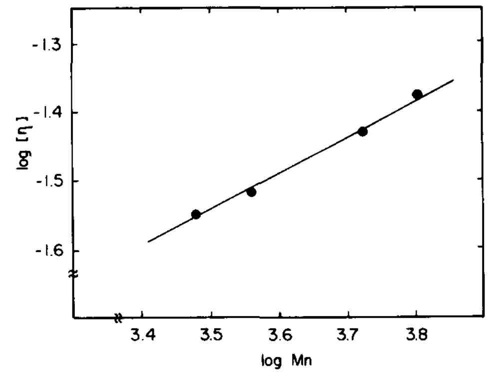


Figure 4 Relation between intrinsic viscosity and number-average molecular weight of poly(allyl cyanide) in CH_2Cl_2 at 25°C

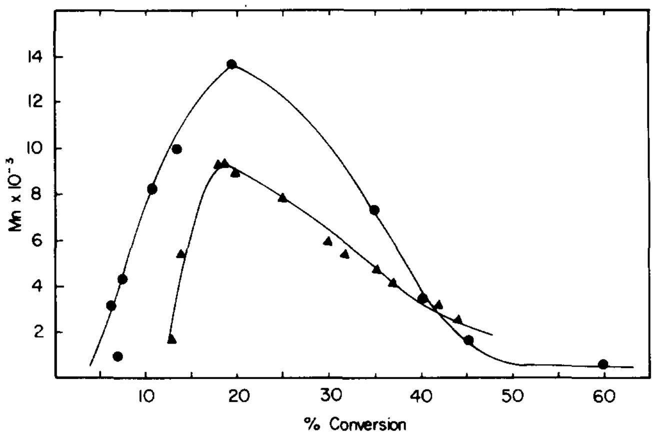


Figure 5 Molecular weight of poly(allyl cyanide): (●) bulk; (▲) containing 0.1 mol% $ZnCl_2$

bulk is about 1.4×10^4, whereas for $ZnCl_2$-containing monomer the molecular weight decreases noticeably and varies with the amount of $ZnCl_2$. This observation is not in agreement with results reported for allyl alcohol[3]. In order to understand the effect better, more investigations have to be made into the nature of complex formation of allyl compounds with metal halides.

The polymers obtained by irradiation in air were oily viscous products of low molecular weights, which could not be determined by the viscosity method.

Infra-red spectral analysis

The i.r. spectra of monomer and polymers obtained under different conditions are given in *Figure 6*. In the spectrum of monomer (*Figure 6a*), the peaks at 1400 and 2250 cm^{-1} correspond to $-C{\equiv}N$; the peaks at 1650, 990 and 900 cm^{-1} to $-C{=}C-$ double bond; and the weak peaks around 3500 and 3000 cm^{-1} to pendant $-C{=}N-H$ groups, which are formed by resonance and proton transfer. In the i.r. spectrum of radiation-induced polymer (*Figure 6b*), the peaks corresponding to $-C{=}C-$ double bonds disappear, but the peaks of $-CN$ are retained. The peaks for $-CH_2-$ groups appear around 1500 and 1300 cm^{-1} as broad peaks. Therefore polymerization by radiation proceeds by addition to $-C{=}C-$ double bonds with repeat units of $-CH_2-CH(CH_2CN)-$. Some $-CH(CH_3)CH(CN)-$ repeat units also exist due to molecular rearrangements.

The i.r. spectrum of polymer obtained by a chemical catalyst is different from that of radiation-induced polymer. In this case (*Figure 6c*), the broad peak at about 1450 cm^{-1} shows the presence of $-CH_3$ groups on a chain backbone. The $-CH_2-$ peaks contribute more to $-C{=}N-H$ at 3000 cm^{-1}, and $-CN$ peaks at 2250 and 1650 cm^{-1} become very weak. The repeat unit in the polymer chain is most probably $-CH(CH_3)-CH(CN)-$. This result substantiates the polymer structure reported by Nakayama *et al.*[5].

Nuclear magnetic resonance spectral analysis

The ^1H n.m.r. and ^{13}C n.m.r. spectra of monomer and radiation-induced polymer in DMSO-d_6 are shown in *Figures 7* and *8*, respectively. In the ^1H n.m.r. spectrum of monomer (*Figure 7a*) the peaks are assigned as follows: $CH_2{=}CH$ at 5–6 ppm; $-CH_2-$ at 3.0–3.5 ppm. The small peaks at about 2 and 2.5 ppm correspond to $-CH_2-$ and $-CH_3$ formed by resonance and proton shift. In the ^1H n.m.r. spectrum of poly(allyl cyanide) (*Figure 7b*), the peaks corresponding to the allyl groups (5–6 ppm) have completely disappeared. The $-CH_2$ (as $-CH_2CN$) peak remains unchanged, with a small shift to a higher (centred at 3.5 ppm) value in the spectrum of the polymer. The broad peaks in the range 1.5–3.0 ppm are typical of

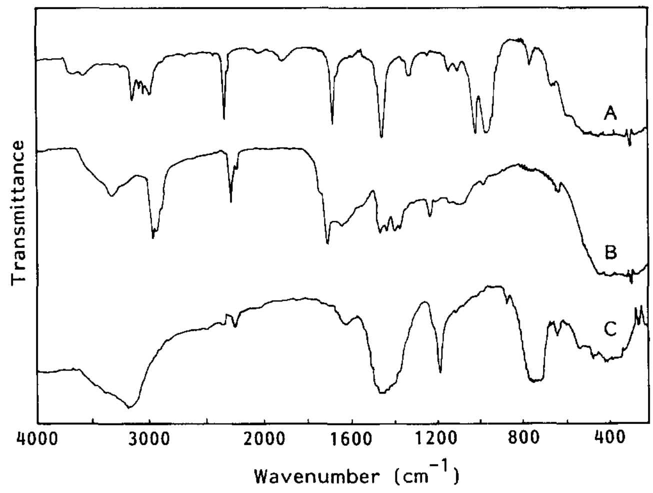


Figure 6 I.r. spectra of allyl cyanide: (a) monomer; (b) polymer by radiation; (c) polymer by n-BuLi

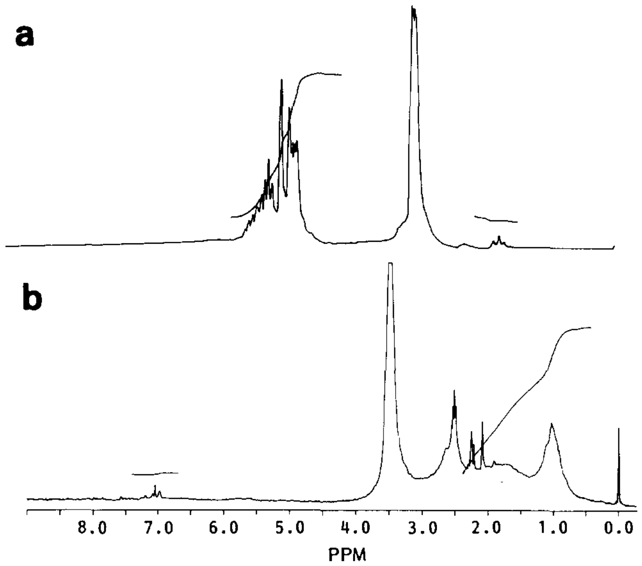
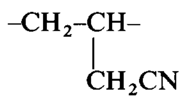


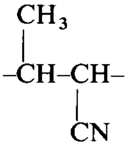
Figure 7 The 80 MHz ^1H n.m.r. spectra of allyl cyanide: (a) monomer; (b) polymer in DMSO-d_6

polymers and they are assigned to $-CH_2-$ and $-CH-$ groups in the polymer chain. The broad $-CH_3$ peak centred at 1.0 ppm indicates the presence of repeat unit (II) in addition to the main repeating unit (I). The $-CH_3$ groups are also present at the end of chains made of unit (I). The evidence for repeat unit (I) in the polymer chain is the unchanged peak of $-CH_2CN$ and the formation of new peaks corresponding to $-CH_2-$ and $-CH-$. The $-CH_2CN$ and $-CH_2-$ groups do not exist in repeat unit (II)



$$-CH_2-\underset{CH_2CN}{\underset{|}{C}}H-$$

(I)



$$-\overset{CH_3}{\overset{|}{C}}H-\underset{CN}{\underset{|}{C}}H-$$

(II)

The structure of the product was investigated further with ^{13}C n.m.r. to observe any possible changes in $-CN$. The monomer spectrum of *Figure 8a* includes peaks corresponding to $-CN$ at 118.2 ppm, $H_2C{=}$ at 118.9 ppm, $=CH-$ at 127.9 ppm and $-CH_2-$ at 21.3 ppm. The weak peaks at 38–44 ppm are those of the solvent, DMSO-d_6. In the spectrum of the polymer (*Figure 8b*) the $=CH-$ peak at 127.9 ppm is not observed. This shows the absence of $=CH-$ groups in the polymer chain. The $H_2C{=}$ peak at 118.9 ppm, which is superimposed on the peak of $-CN$ in the monomer spectrum, disappeared in the polymer spectrum, causing an intensity reduction. Other peaks in the polymer spectrum correspond to $-CH_2-$ at 33.5 and 22.1 ppm, $-CH-$ at 17.4 ppm and $-CH_3$ at about 15 ppm. All the peaks in the polymer spectrum are weak, and broad, which is typical for polymers. The solvent (DMSO-d_6) peaks are centred at about 40 ppm. The ^{13}C n.m.r. results also show the main repeat unit in the polymer is unit (I). This result is in good agreement with the structure determined by ^1H n.m.r. and i.r.

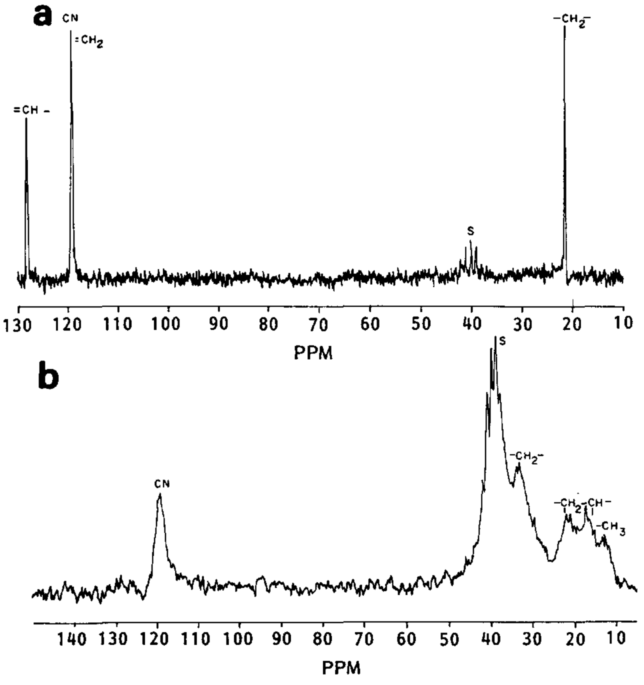
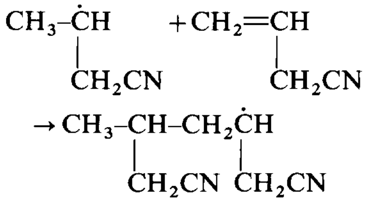


Figure 8 The 20.13 MHz ^{13}C n.m.r. spectra of allyl cyanide: (a) monomer; (b) polymer in DMSO-d_6

For a free-radical mechanism, the proton addition or abstraction will be as:

$$(H^\cdot)+CH_2{=}CH{-}CH_2{-}CN$$
$$\rightarrow CH_3{-}\dot{C}H{-}CH_2CN$$
$$\rightarrow (H_2)+CH_2{=}CH{-}\dot{C}H{-}CN$$

The second radical is resonance-stabilized and does not contribute to the polymerization. However, the first radical is reactive towards polymerization and gives:



$$CH_3{-}\underset{CH_2CN}{\underset{|}{\dot{C}}}H + CH_2{=}\underset{CH_2CN}{\underset{|}{C}}H \rightarrow CH_3{-}\underset{CH_2CN}{\underset{|}{C}}H{-}CH_2\underset{CH_2CN}{\underset{|}{\dot{C}}}H$$

This mechanism is well substantiated by i.r. and n.m.r. spectral data, and dipole moment measurements.

The ionic reactions of allyl compounds usually give proton transfer and rearrangements in the molecule. This type of change gives the repeat unit (II) and also pendant groups of $-C{=}N{-}H$, which were observed in i.r. spectra.

Dipole moments of poly(allyl cyanide)

The mean-square dipole moment per repeat unit of radiation-induced polymer was determined from the Guggenheim–Smith equation[7,8]:

$$\frac{\langle\mu^2\rangle}{x}=\frac{27kTM}{4\pi N_A d_1}\left(\frac{(d\varepsilon/dw)_{w\to 0}}{(\varepsilon_1+2)^2}-\frac{2n_1(dn/dw)_{w\to 0}}{(n_1^2+2)^2}\right)$$

where $\langle\mu^2\rangle$ is the mean-square dipole moment of the chain; x the number of repeat units; M the molecular weight of the repeat unit; N_A Avogadro's number; k Boltzmann's constant; T the absolute temperature; d_1 density of solvent; ε and ε_1 the dielectric constants of solution and solvent, respectively; w the weight fraction of polymer; n and n_1 the refractive indexes of solution and solvent, respectively.

The density and refractive index of a solvent at a specified temperature were taken from reported data[9]. The measured and calculated results for poly(allyl cyanide) obtained by radiation polymerization are tabulated in *Table 1*. The mean-square dipole moment is reduced to a dimensionless, dipole moment ratio D_∞ by the relation:

$$D_\infty=\lim_{x\to 0}\frac{\langle\mu^2\rangle}{x\mu_0^2}$$

where μ_0 is the dipole moment of saturated monomer molecule. The D_∞ value is always smaller than unity due to the restrictions on internal rotation in the chain. However, it approaches unity for flexible chains. The D_∞ value for poly(allyl cyanide) at 20–50°C changes between 0.76 and 0.89. These values are higher than the expected values from the high polarity of the CN groups (e.g. $\mu_0=3.60$ D for n-butyronitrile). For example, the D_∞ of poly(*p*-chlorostyrene) is 0.5–0.6[10] although the polarity of the C–Cl bond is lower ($\mu_0=2.00$ D for *p*-chloromethylbenzene). The high D_∞ for poly(allyl cyanide) is most probably because of the possibility of internal rotation due to the presence of extra $-CH_2-$ groups in the side-chain, which increases the flexibility compared to poly(*p*-chlorostyrene).

Table 1 Results of dipole moment measurements[a]

Temperature (°C)	20.0	30.0	35.0	40.0	45.0	50.0
ε_1	2.394	2.359	2.347	2.339	2.326	2.315
$(dn/dw)_{w\to 0}$	0.094	0.081	0.084	0.073	0.065	0.060
$(d\varepsilon/dw)_{w\to 0}$	22.53	21.23	20.31	18.23	18.99	20.33
$\langle\mu^2\rangle/x$ (D^2)	11.14	11.05	10.77	9.88	10.54	11.54
D_∞	0.86	0.85	0.83	0.76	0.81	0.89

[a] $\mu_0 = 3.60$ D for n-butyronitrile[11]

Table 1 shows that D_∞ values decrease slightly in the 20–40°C range, but increase more rapidly at 40–50°C, with a minimum at 40°C. Similar behaviour was reported for poly(methyl methacrylate) in benzene[12]. The change can be attributed to a conformational transition between two intramolecular states characterized by different short-range interactions. Further work is needed to explain the nature of this transition in detail.

The investigation of the dipole moment for the polymer obtained by chemical catalysis might be interesting because the polymer has $-CH_3$ as a side-group in addition to directly attached –CN group to the backbone. However, this polymer was insoluble in non-polar solvents and could not be studied.

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