An n.m.r. investigation of structure and motion in hydrated α,ω-dicarboxylatopolybutadiene*

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N.m.r. analysis of the hydration and temperature behaviour of resolved carboxyl carbon resonances in the acid and neutralized α,ω-dicarboxylatopolybutadiene telechelics reveal a complex interaction between water and chain end groups participating in the formation and subsequent stability of crosslinks. A multiplicity of environments are detected above the glass transition of the host polymer matrix arising from chemical and physical inequivalences. Reasonable interpretations are advanced to account for the observed carboxyl peaks. Analysis of the temperature dependence of ^{13}C linewidths offers further insight into the manner in which end groups influence overall motion in the polymer. Extraction of meaningful activation energies from ^{13}C linewidth data, however, must take correlation frequency distributions into account. The anomalous behaviour of water and its influence on structure and motion is explored.

(Keywords: n.m.r.; α,ω-dicarboxylatopolybutadiene; telechelics)

INTRODUCTION

Telechelics which are formed when a polymer chain is terminated at both ends with an ionic group are useful model systems in the overall investigation of ionomers. A recent n.m.r. study[1] on acid- and zirconium (Zr)-neutralized α,ω-dicarboxylatopolybutadiene in the nominally dry state, explored the qualitative features of structural crosslinks involving end groups and their influence on molecular motion. The resolved carboxyl resonances gave site-specific information on the chain dynamics at the crosslink itself. The collated n.m.r. data pointed to thermoreversible crosslink formation with evidence of a partial break-up of the crosslink at high temperatures. Data interpretation is complicated by inevitable trace amounts of water in the samples. Clearly it is important to understand the role of water in these systems, first to clarify data interpretation and, second, because of the important role that water plays in achieving the remarkable permselective properties of ionomers[2]. This paper focuses principally upon hydration effects in the Zr-neutralized polymer.

EXPERIMENTAL

Samples

The α,ω-carboxylatopolybutadiene acid, PBH(M_n), and its Zr-neutralized form, PBZr(M_n), with molecular weights (M_n) of 1900 and 4600, respectively, are described fully in an earlier paper[1]. The 4 wt% carboxyl carbons in the Irganox stabilizer used in preparing the telechelics make a negligible contribution to the carbon spectra. Hydration of PBZr was achieved by soaking in distilled water for >1 week: water content was determined from the decrease in weight after drying the sample at 370 K for 2–4 days until no further weight loss was registered. Water content, W, denotes wt% relative to 100 wt% of the dry sample. Hydrated samples are designated PBZr(M_n:W).

N.m.r. experiments

Solid-state ^1H and ^{13}C n.m.r. experiments were carried out on a Bruker MSL300 spectrometer operating at 300 MHz for protons and 75.5 MHz for carbons. High-resolution solid-state ^{13}C n.m.r. spectra were observed under magic angle spinning (MAS) at ~3.8 kHz and high power decoupling in one of two ways: either by cross-polarization (CP) with contact times of 1.2 ms or by the single 90° pulse method. The radio frequency (r.f.) field strength for both ^1H and ^{13}C was 53 kHz. ^{13}C

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chemical shifts are reported in ppm using the methine carbon of adamantane (29.5 ppm relative to TMS) as an external reference. Proton T_1, T_2 and $T_{1\rho}$ values were measured in the usual way with a broad-line probe[3]. The Bruker B-VT1000 temperature controller was accurate to ± 1 K.

To avoid water loss during measurements on hydrated samples, n.m.r. data as a function of temperature were recorded as expeditiously as possible: 6–8 h per sample for ^{1}H broad-line T_1, T_2 and $T_{1\rho}$s and ~40 h for ^{13}C CP/MAS n.m.r. data. Measurements at high water contents were avoided in this study because of the likelihood that the large centrifugal force from rapid spinning may redistribute or assist in the removal of part of the absorbed water. Weight loss (water loss) during the ^{13}C CP/MAS experiments was 2–4% for samples with high water content and <1% for samples with <10 wt% water.

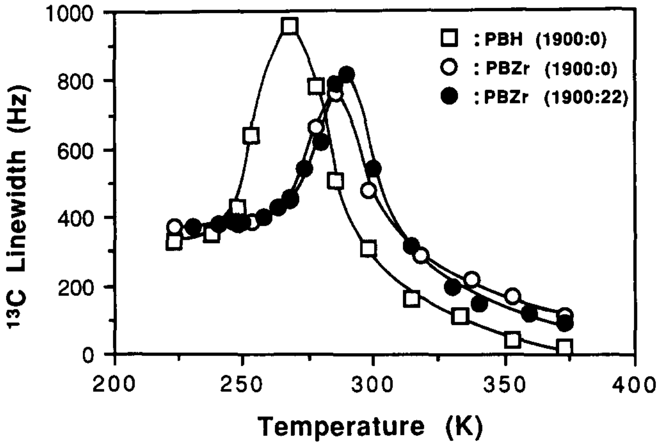

Figure 2 ^{13}C linewidth *versus* temperature for the resonance line at 143 ppm

RESULTS AND DISCUSSION

^{13}C spectra

Linewidths. The most notable feature of the variable temperature CP/MAS spectra for PBZr(1900:22), presented in *Figure 1*, is the dependence of linewidth on temperature: the relatively narrow lines at low temperatures first broaden as temperature is increased and then narrow again. Collated linewidth data for ^{13}C resonances at 143 ppm are shown in *Figure 2* for PBH(1900:0), PBZr(1900:0) and PBZr(1900:22). Similar results have been observed for the peak at 115 ppm. Broadening occurs when molecular motion produces magnetic fields fluctuating at frequencies close to the r.f. decoupling field (in this instance, 53 kHz), which diminishes the modulation of ^{13}C/^{1}H dipolar interactions. The effect on chemical shift anisotropy is small. Subsequent line narrowing at still higher temperatures occurs when molecular motions become too fast to interfere with r.f. decoupling and the distribution of the isotropic chemical shift is averaged by fast molecular motions[4,5]. An equation that has been used to analyse the temperature dependence of ^{13}C linewidths is that of Takegoshi and Hikichi[6]:

$$\delta = \delta_o + \delta_1(2/\pi)\arctan[\alpha(T_o - T)] + \lambda M_2 J(\omega_1, \tau) \quad (1)$$

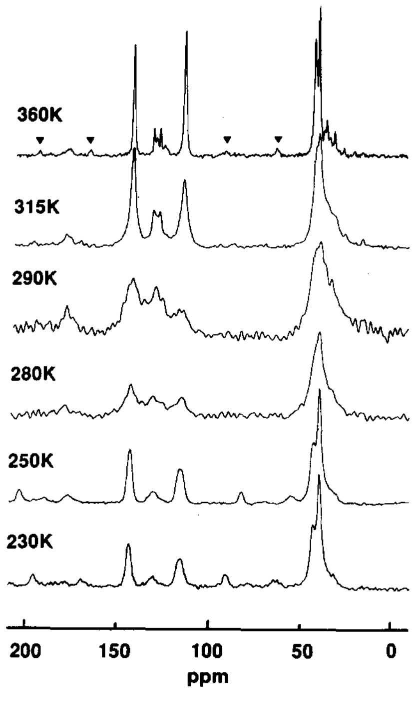

Figure 1 ^{13}C CP/MAS spectra of PBZr(1900:22) at the temperatures shown. The position of spinning sidebands (▼) are typically illustrated for the spectrum at 360 K. Sideband intensities at 280 and 290 K are too low to be detected (see text)

The first term represents the intrinsic linewidth, accounting for various temperature-independent line-broadening mechanisms. The second term is an empirical description of a supposed change in the distribution of isotropic chemical shifts with temperature, and the last term is a better-founded representation of the life-time broadening that results when the decoupling rate, given by ω_1, is comparable to some characteristic frequency of molecular motion that modulates the ^{13}C–^{1}H dipolar interaction. M_2 is the powder-averaged second moment of this dipolar interaction, and λ is the fraction of this moment that is time-dependent. Motional modulation of the carbon chemical shifts produces broadening that is similar in form but it is expected that the dipolar contribution is dominant. This assignment is consistent with the observation that all carbons experience about the same broadening, regardless of chemical shift anisotropy, etc. As emphasized by VanderHart and coworkers[7], the last term in equation (1) is a reflection of $T_{1\rho}$ and, roughly speaking, samples the spectral density, $J(\omega_1, \tau)$, of molecular motions at ω_1.

In earlier analyses, $J(\omega_1, \tau) = \tau/(1 + \omega_1^2\tau^2)$ and the correlation time τ is assumed to have an Arrhenius dependence on temperature, $\tau = \tau_o \exp(E_a/RT)$, where E_a is the activation energy and τ_o is the correlation time at infinite temperature. Fitting equation (1) to the experimental data for PBH(1900:0), PBZr(1900:0) and PBZr(1900:22) yields the parameters listed in *Table 1* from which a number of conclusions can be drawn:

- The reduction parameter λ decreases with neutralization but less so with subsequent hydration, indicating that the motions become progressively more anisotropic due to restrictions induced by crosslink formation.
- The onset temperature of the transition at which motions set in, T_o, increases by 15–20 K upon neutralization and a further 5 K with subsequent hydration.
- Neutralization and subsequent hydration cause the

Table 1 Parameters obtained from the ^{13}C linewidth *versus* temperature for PBH(1900:0), PBZr(1900:0) and PBZr(1900:22). Correlation frequency distributions are neglected in this analysis

Samples	E_a (kJ mol^{-1})	$\ln \tau_0$	λ	T_0 (K)	δ_0 (Hz)	δ_1 (Hz)
PBH(1900:0) (143 ppm)	40	−28.8	0.46	240	130	120
PBZr(1900:0) (143 ppm)	30	−23.8	0.32	255	140	130
PBZr(1900:22) (143 ppm)	27	−24.2	0.39	260	140	125
PBH(1900:0) (115 ppm)	44	−23.9	0.27	240	180	160
PBZr(1900:0) (115 ppm)	36	−23.7	0.22	260	210	190
PBZr(1900:22) (115 ppm)	30	−20.4	0.23	265	210	185

computed E_a values apparently to decrease. Note, however, that the third term in equation (1) inadequately describes the broad correlation frequency distributions which are undoubtedly present in these systems.

Recall that the ^{13}C linewidths, identified here as the width at half-height of the resonance line, do not portray the subtleties of correlation time distributions in polymers and, in such circumstances, it is invariably necessary to correct the apparent E_a to higher values to an extent defined by the nature of the distribution in each case[8,9]. In this and other studies reported in the literature[6], E_a values computed from equation (1) which ignore such distributions offer little direct insight into the dynamics of motions in systems where broad distributions of correlation frequencies are prevalent.

Carboxyl carbon resonances. The behaviour of chain end groups in the crosslinks can be monitored via the chemical shift of the carboxyl carbon resonance (*Figure 1*). A significant body of published data demonstrate the sensitivity of carboxyl groups to their local environment[10]. At low temperatures there is a problem of overlapping resonances involving the broad distribution of spinning sidebands, compounded by instrumental limitations on available MAS rates which, collectively, made it difficult to detect the carboxyl carbon resonance below 270 K. Furthermore, because the intensities of the resonances are low, techniques such as TOSS or dipolar dephasing cannot be exploited to any great effect[3]. At higher temperatures, the linewidths of the main resonances at 143 and 115 ppm broaden (*Figure 1*) and, accordingly, their spinning sidebands are weak. Also, the distribution of anisotropic chemical shifts tends to narrow with further increase in temperature, thus facilitating detection of the carboxyl carbon resonances.

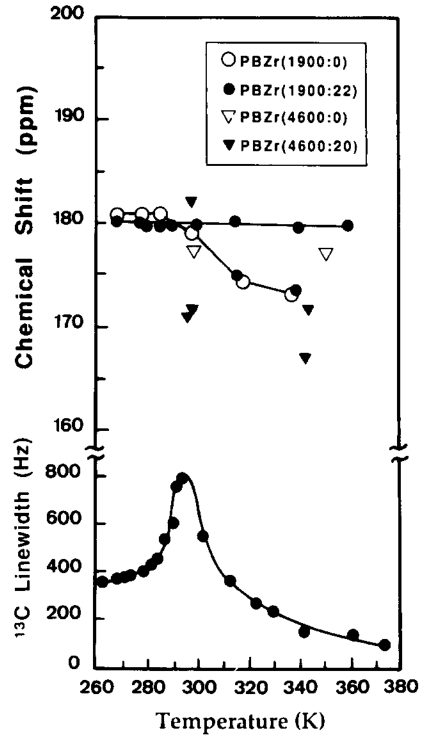

Figure 3 Temperature dependence of the carboxyl carbon chemical shifts recorded under CP/MAS for the samples indicated. ^{13}C linewidth data for PBZr(1900:22) are reproduced from *Figure 2* (see text)

The collated chemical shift data, recorded under CP/MAS, for the carboxyl carbon resonances of both dry and hydrated PBZr(1900) and PBZr(4600) are shown in *Figure 3*. Also included is the ^{13}C linewidth dependence on temperature for PBZr(1900:22). In interpreting data for the neutralized and hydrated polymer, recall that the exchanged Zr ions in the polymer are primarily coordinated by water in the first hydration shell, rather than the carboxyl groups[11], which supports the view that water bridges involving Zr, water and the carboxylate end groups are formed. As the water concentration increases and the Zr hydration saturates, the carboxyl carbons increasingly sense only a water environment. Thus, for example, in PBZr(1900:22), there is virtually no change in the chemical shift of the main carboxyl resonance near 180 ppm which is consistent with a sustained interaction of carboxyl groups with water up to 360 K. One of the peaks in the wet and nominally dry PBZr(1900) polymer, shifts upfield with increasing temperature, mimicking the behaviour of the minor acid proton peak reported earlier[1]. Recall that the shift was tentatively attributed (1) to the progressive dehydration of the carboxylate moiety on the assumption that the polymer was not completely dry and, specifically, that the crosslinks were initially hydrated and/or (2) to the dissociation of the ion–ion interaction within the crosslinks along with (3) a change in the molecular motion of the carboxyl carbons. It is most probable that at least part of the hydrated polymer preferentially dehydrates between 300 K and 375 K, ultimately resulting in a reco-ordination of the carboxyl group with Zr, leading in turn to the anticipated upfield peak in the temperature region wherein the crosslink begins to break down[1].

The behaviour of end groups leads to surprisingly broad anisotropic chemical shift distributions in PBZr(1900) even at high temperatures: spinning sidebands of resonances at 143 and 115 ppm are still observed at 360 and 373 K. The carboxyl carbon resonance of PBZr(1900:0) cannot be observed either by CP/MAS or single pulse procedures with a short repetition time of 3 s at high temperatures, in the region of 373 K. This is due to end-group dissociation at high temperatures, as proposed earlier[1], leading to increased mobility and a concomitant reduced facility to cross-polarize carboxyl carbons. $T_1(^{13}C)$ for the end groups remains long which precludes detection of the minor resonances with a single 90° pulse using a 3 s repetition time. This is consistent with the conclusions of the earlier paper that the crosslink breaks down at higher temperatures as evidenced principally by the formation of the proton $T_{1\rho}$ minimum at ~360 K[1]. That the carboxyl resonance is still observed in the CP/MAS spectrum of PBZr(1900:22), even at 360 K, offers supporting evidence for the role of water bridges in the formation of crosslinks, as alluded to earlier.

Clearly, the presence or absence of water in different parts of the polymer contributes to the observed distribution of carboxyl group environments. It is interesting to note the correlation between the appearance of multiple carboxyl peaks followed by the subsequent breakdown of the crosslink and the onset of the polymer matrix glass transition in the region of 300 K on the n.m.r. time-scale (*Figure 3*).

On average, PBZr(4600) is more mobile because there are a greater number of PB chain units between crosslinks. This is reflected in ^{13}C spectra of both dry, PBZr(4600:0), and hydrated, PBZr(4600:20), polymer using the single 90° pulse method (*Figure 4*). Linewidths are narrower and the end-group carboxylate carbon resonance is commensurately weaker. End-group behaviour in PBZr(4600:20) is quite different from that observed in PBZr(1900:22). The chemical shift of the carboxyl carbon resonance in dry PBZr(4600:0) changes little from 298 to 353 K which contrasts with observations in PBZr(4600:20) where events are more complex (*Figure 5*). The carboxyl carbons already exhibit extensive mobility at 253 K, paralleling motions in the polymer as a whole. This is revealed in proton linewidth results which indicate the onset of general motions on the T_2 time-scale at ~200 K in both wet and dry polymer[1]. Again a range of carboxyl group environments is inferred. At 298 K, peaks appear in the hydrated polymer at 183.0, 171.9 and 170.7 ppm; at 353 K peak positions are at 172.5 and 167.5 ppm (*Figures 3* and *5*). A translation of the chemical shift data for PBZr(4600) by ~60 K to higher temperatures brings them into rough coincidence with the data for PBZr(1900). The shift denotes the approximate difference in the glass transition temperature (T_g) for the two polymers as revealed in T_2 data. Inevitable variations between the two sets of results are expected when it is recalled that 20 wt% hydration in PBZr(4600:20) is about twice the degree of hydration in PBZr(1900:22) relative to the ionic groups because of differences in molecular weights.

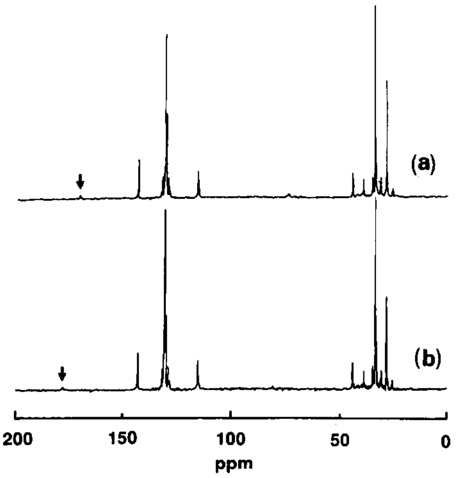

Figure 4 ^{13}C spectra for (a) PBZr(4600:20) and (b) PBZr(4600:0) polymer using a single 90° pulse at 298 K

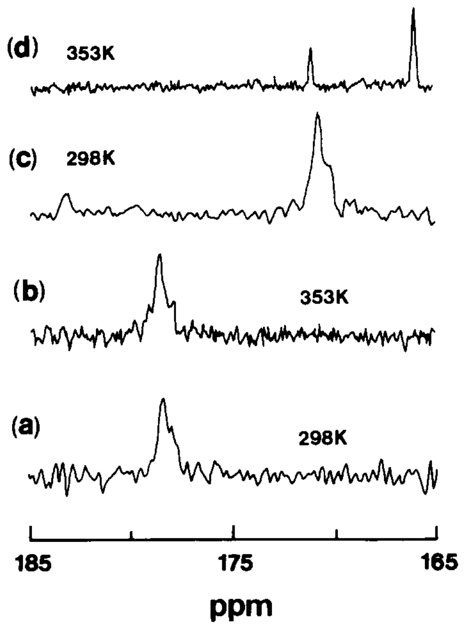

Figure 5 ^{13}C spectra of the carboxylate carbon resonance of PBZr(4600:0) at (a) 298 K and (b) 353 K and of PBZr(4600:20) at (c) 298 K and (d) 353 K

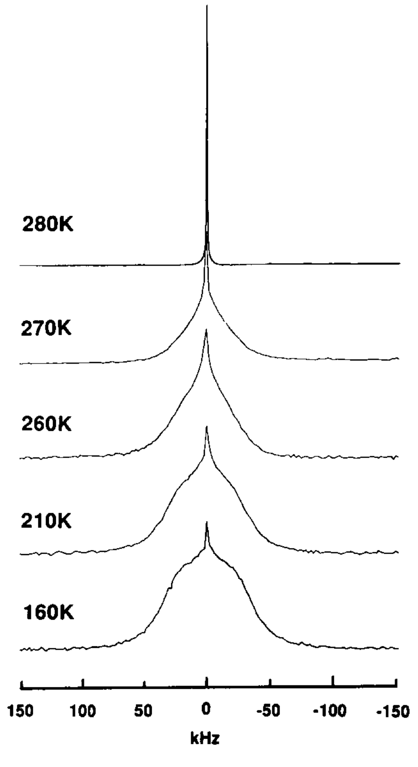

Figure 6 ^1H spectra of PBZr(1900:32) at the temperatures indicated

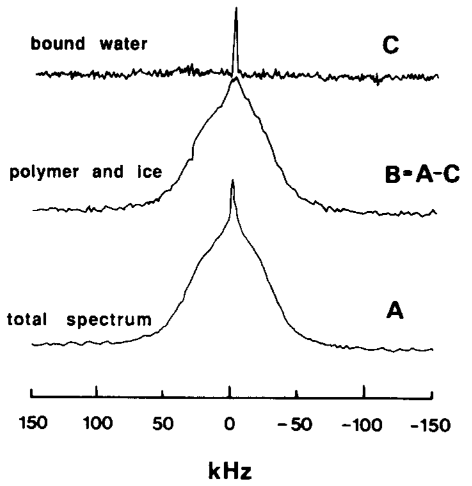

Figure 7 ^{1}H spectra at 210 K of (A) PBZr(1900:35), (C) bound water in PBZr(1900:35) and (B) the difference spectrum, (A)−(C)

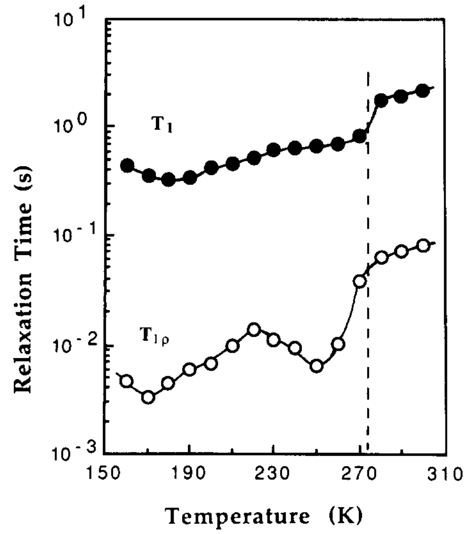

Figure 8 $T_1(^1H)$ and $T_{1\rho}(^1H)$ water signal in PBZr(1900:32)

^{1}H relaxation studies

The anomalous behaviour of water in host matrices, of which the systems under current examination are examples, influences the overall response of the hydrated polymer. Upon hydration, the system becomes rather complicated. Besides the multiple polymer components, there are also several kinds of water present which include tightly bound water, loosely bound water, associated water and ice below 273 K. Proton linewidths are especially useful in identifying the different types of water present[3]. Linewidth data for PBZr(1900:32), given as a function of temperature in *Figure 6*, reveal the presence of mobile water down to ~160 K which is the lower limit of our temperature measurements. This mobile component signifies tightly bound water which undergoes a glass-like transition with a T_g which typically can be in this temperature region. In the case of PBZr, it denotes water which is associated with the end groups.

The difference in T_1 values for the broad and narrow parts of the line can be exploited to observe the two resonances separately, as shown in *Figure 7*. T_1 and $T_{1\rho}$ minima corresponding to the T_g transition of bound water, which are associated with the narrowest linewidth component below 273 K, were observed, respectively, at 180 and 170 K (*Figure 8*). As the normal freezing point of water is approached, both relaxation times increase sharply indicating the presence of a significant amount of near-normal water. It is not unusual for such water to act as a plasticizer[3].

CONCLUSIONS

The hydration and temperature behaviour of resolved carboxyl carbon resonances in the acid and neutralized α,ω-dicarboxylatopolybutadiene telechelics reveal a complex interaction between water and chain end groups participating in the formation and stability of crosslinks. A multiplicity of environments are created above the glass transition of the host polymer matrix arising from chemical and physical inequivalences. Reasonable interpretations are advanced to account for the observed carboxyl peaks. Analysis of the temperature dependence of ^{13}C linewidths offers further insight into the manner in which end groups influence overall motion in the polymer. Neutralization strengthens the network in the sense that it survives to higher temperatures in the thermoreversible breakdown process proposed in an earlier investigation[1]. Extraction of E_a values from ^{13}C linewidth data must be approached with caution. Analyses which do not take correlation frequency distributions into account (as are prevalent in this and other systems reported in the literature) will predict E_a values that are too low. In the absence of such distribution considerations, interpretation of the observed decrease in E_a with neutralization and subsequent hydration denotes enhanced motional heterogeneity rather than an activation process which is more facile. The anomalous behaviour of water and its influence on structure and motion have been explored.

REFERENCES

1 McBrierty, V. J., Douglass, D. C., Zhang, X., Quinn, F. X. and Jérôme, R. *Macromolecules* 1993, **26**, 1734
2 Pineri, M. and Eisenberg, A. (Eds) 'Structure and Properties of Ionomers', Reidel, Dordrecht, 1987
3 McBrierty, V. J. and Packer, K. J. 'Nuclear Magnetic Resonance in Solid Polymers', Cambridge University Press, Cambridge, 1993
4 Suwelack, D., Rothwell, W. P. and Waugh, J. S. *J. Chem. Phys.* 1980, **73**, 2559
5 Rothwell, W. P. and Waugh, J. S. *J. Chem. Phys.* 1981, **74**, 2721
6 Takegoshi, K. and Hikichi, K. *J. Chem. Phys.* 1991, **94**, 3200
7 VanderHart, D. L., Earl, W. L. and Garroway, A. N. *J. Magnetic Res.* 1981, **44**, 361
8 McBrierty, V. J. and Douglass, D. C. *Phys. Rep.* 1980, **63**, 61
9 Beckmann, P. A. *Phys. Rep.* 1988, **171**, 85
10 Bovey, F. A. 'Nuclear Magnetic Resonance Spectroscopy', 2nd edn, Academic Press, New York, 1988
11 Boyle, N. G., Coey, J. M. D., Meagher, A., McBrierty, V. J., Nakano, Y. and MacKnight, W. J. *Macromolecules* 1984, **17**, 1331