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Microstructure determination of poly (*trans*-4-acryloyloxyazobenzene) by n.m.r. spectroscopy

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The microstructure of poly(*trans*-4-acryloyloxyazobenzene) P(AB) homopolymer, prepared by solution polymerization using AlBN as initiator is analysed by one- and two-dimensional NMR spectrotcopy. Sequence distribution was calculated from ^{13}C{^{1}H}n.m.r. spectrum of the homopolymer. A ^{13}C distortionless enhancement by polarization transfer spectrum was used to differentiate between the resonance signals of methine and methylene units in the homopolymer. The triad sequence distribution of poly(*trans*-4-acryloyloxyazobenzene) P(AB), determined from carbonyl resonance of the homopolymer, is in good agreement with the triad concentrations calculated from the Bernoullian statistical model. 2D heteronuclear single quantum correlation (HSQC) and correlated spectroscopy (COSY) spectroscopy was used to analyse the complex ^{1}Hn.m.r. spectrum. Homonuclear 2D TOCSY n.m.r. spectroscopy was used to ascertain the various configurational sequence of the poly(*trans*-4-acryloyloxyazobenzene) P(AB) homopolymer. 2D NOESY experiment was carried out to determine one of the many probable conformations of the homopolymer in solution state. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: n.m.r. spectroscopy; microstructure; homopolymer)

INTRODUCTION

The photomechanical, photoviscosity effects and pH control systems of photoresponsive polymers are important by themselves and have possible commercial applications. Photoresponsive polymers are used in constructing photoactive devices in several fieids such as printing, photocopying, photolithography and photosensors[1]. It is well known that n.m.r. spectroscopy is probably the most effective method for characterizing the configurational structure of polymers, because the chemical shift is sensitive to configurational sequences[2,3]. Two-dimensional (2D) n.m.r. experiments[4,5] have been used as the most reliable method for determining the conformational[6–8] and configurational[9] microstructure of the copolymers. Milos *et al*.[10] used 2D n.m.r. spectroscopy for the characterization of poly(*t*-butyl acrylate). The photo and thermal isomerization of optically active polymers containing side-chain photochromic groups has been the subject of thorough investigation aimed at establishing useful correlation between photochromic properties and structural parameter.

In this respect when dealing with optically active systems, chiroptical technique have been fruitful and in some cases they have been suggested the occurrence of an extensive rearrangement of polymer conformation. The photoisomerization of polymeric *trans* azo compound was initially studied by Morawetz and coworkers[11] who first demonstrated that such provide the opportunity to observe what effect an azo linkage incorporated into the chain would have as compared to their corresponding low molecular weight analogues.

A photoresponsive synthetic polymer is a speciality polymer having photoreceptor chromophores which can transfer light energy into a change in the conformation of the polymer. The basic idea for controlling properties of polymers by photoirradiation is to use photoresponsive trigger molecules[12]. Blair *et al*.[13] described photoresponsive effects in photochromic polyamides in which every monomer unit contains an azo group. It is well known, however, that polymer conformational properties definitely depend on the main-chain tacticity. Therefore, in order to get a better insight into the polymer photochromism, it is desirable to start a systematic investigation of photochromic polymer stereochemistry by ^{13}Cn.m.r. This technique is able to provide macromolecular dynamics and the main-chain tacticity[14,13]. ^{13}Cn.m.r spectroscopy was used to analyse the radical polymer of *trans*-4-methacryloyloxy azobenzene (MAB) with menthyl methacrylate[15].

In the present paper the result obtained from the ^{13}C{^{1}H}n.m.r. investigation of the radical homopolymer of poly(*trans*-4-acryloyloxyazobenzene) is being reported. The complex ^{1}Hn.m.r. spectrum of the homopolymer has been completely assigned to different configurational sequences with the aid of 2D n.m.r. spectroscopy. The 2D HSQC was used to unambiguously assign the methine and methylene protons of the homopolymer. 2D COSY and TOCSY were used to determine the different sequences possible in the polymer chain. The various spatial couplings between the protons of the side-chain and the main-chain backbone of the homopolymer was studied by 2D NOESY experiment.

EXPERIMENTAL

trans-4-Acryloyloxyazobenzene (AB) was synthesized by reacting commercial (Aldrich) *trans*-4-hydroxyazobenzene

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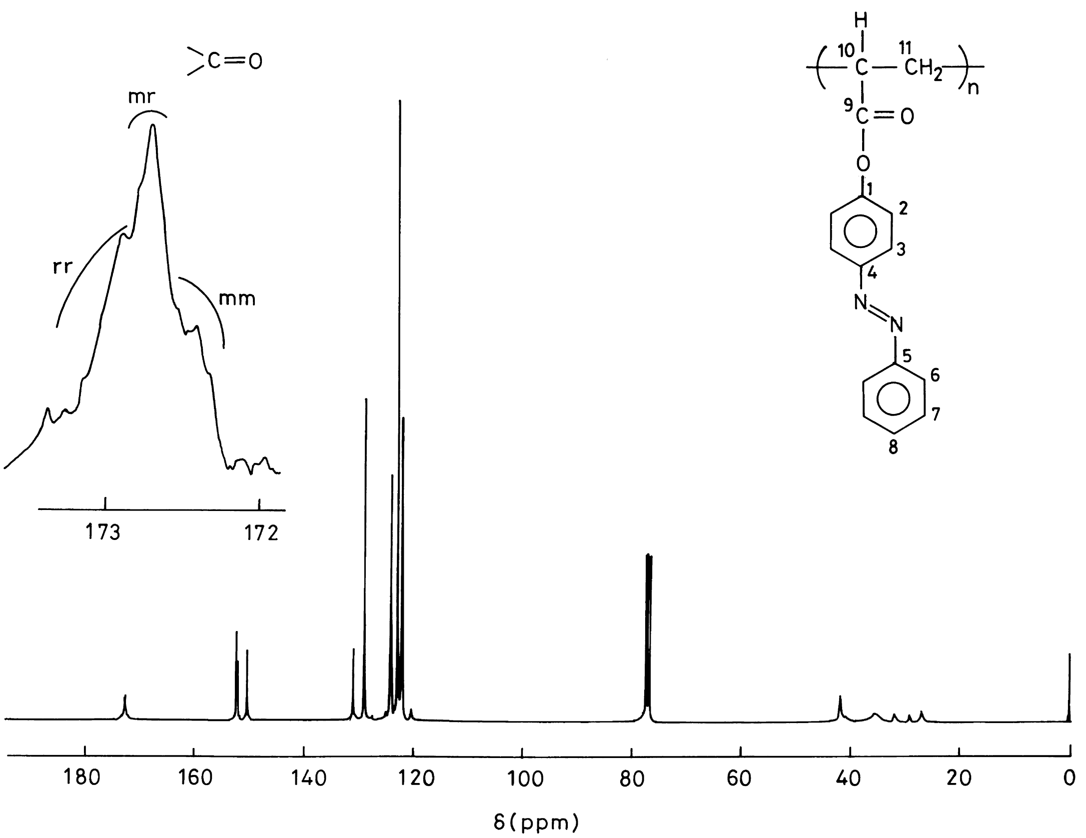

Figure 1 $^{13}C\{^1H\}$n.m.r. spectrum of poly(*trans*-4-acryloyloxyazobenzene) recorded in $CDCl_3$ at 25°C along with the expanded carbonyl ($>$ C=O) region

with acryloylchloride and triethylamine (molar ratio 1:1.5:2) in anhydrous diethylether at room temperature for 8 h. The reaction mixture was extracted with dilute HCl, 5% $NaHCO_3$, and water, in that order and dried over anhydrous Na_2SO_4. The monomer was recrystallized from ethanoll-hexane (1:1).

The poly(*trans*-4-acryloyloxyazobenzene) homopolymer was prepared by solution polymerization using AIBN as initiator in DMF at 65°C for 8 h in a sealed tube. The homopolymer was precipitated in methanol and was reprecipitated using $CHCl_3/CH_3OH$ solvent system. The homopolymer was vacuum dried. The molecular weight of the homopolymer was determined from GPC using polystyrene as narrow standard.

NMR experiments were performed in $CDCl_3$ on Bruker 300 MHz DPX spectrometer at a frequency of 300.13 and 75.5 MHz, for ^1H and $^{13}C\{^1H\}$n.m.r. spectra, respectively. DEPT-135 experiment was carried out at 75.5 MHz in $CDCl_3$ using the standard pulse sequence with a J modulation time of 3.7 ms ($J_{CH} = 135$ Hz) with 2 s delay time. All the two-dimensional experiments were carried out using a BRUKER DPX 300 MHz spectrometer. Two-dimensional proton detected $^1H - {}^{13}C$ heteronuclear chemical shift correlation was recorded in $CDCl_3$ using the standard pulse sequence[16]. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 t_1 experiments. The DQFCOSY experiment, with 32 scans being collected for each t_1 value was carried out in $CDCl_3$. A total of 512 spectra each containing the 1 K data points were accumulated. The nuclear Overhauser effect spectroscopy (NOESY) spectrum was recorded at 350 ms mixing time. Two-dimensional homonuclear total correlation spectroscopy (TOCSY) spectrum was recorded at 4 and 30 ms mixing time. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 t_1 experiments. The details of the Lorentzian shaped curve fitting have been described in our earlier publication [17]. All regressions converged to $x^2 < 1$.

RESULTS AND DISCUSSION

^{13}Cn.m.r. spectrum of poly(*trans*-4-acryloyloxyazobenzene) P(AB) recorded at room temperature in $CDCl_3$ solution is shown in *Figure 1*. The various resonance signals have been assigned using DEPT-135 experiment (*Figure 2*). In the DEPT-135 spectrum,the methine and methyl carbon resonances have positive phase whereas the methylene carbons shows negative phase. The methine carbon resonances around δ 41.0–42.8 , whereas the main-chain methylene carbon resonances around δ 33.5–40.0 . The resonance signals around δ 28.5–29.5 and δ 26.0–27.5 have been assigned to the methyl carbons of the AIBN group attached to the polymer chain ends. From the corresponding methyl protons signal intensity, it is clear that AIBN groups account for a significant proportion in the homopolymer. This means that polymer chains are short having low molecular weight. The number average and weight average molecular weight (M_n and M_w), determined by GPC, of the homopolymer are 3489 and 4260 with polydispersity of 1.22. The methine carbons of the benzene rings which have positive phase in DEPT-135 experiment are assigned around δ 122.0–123.0 . The assignment of the methine carbon resonances of the aromatic side-chain was done in accordance with those reported by Solaro *et al.*[18] for poly(*trans*-4-methacryloyloxyazobenzene). They assigned these resonances by comparing with the model compounds. For PAB, these assignments were also confirmed by

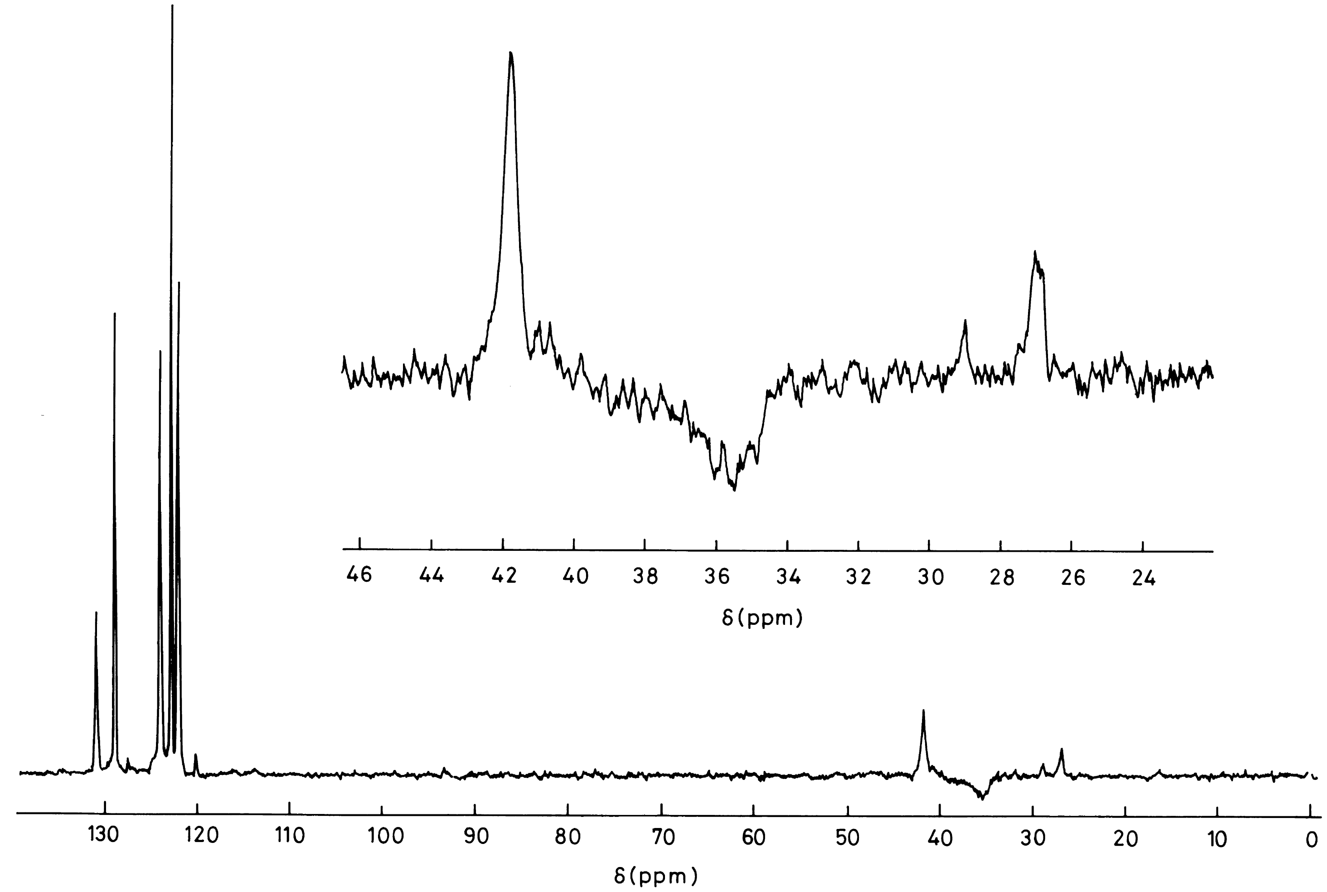

Figure 2 DEPT-135 spectrum of P(AB) recorded in $CDCl_3$ at 25°C along with expanded aliphatic region

quantitative measurement of the methine carbon and proton signals and 2D inverse HETCOR and COSY spectrum. Therefore, the signals at δ 122.16, 124.14, 122.91, 128.97 and 130.97 are assigned to C2, C3, C6, C7 and C8 methine carbon resonances, respectively. The quaternary carbons of the side-chain resonances around δ 150.0–153.0 . All these assignments are shown in *Table 1*, along with their chemical shift values.

The carbonyl carbon of the homopolymer shows multiplet around δ 172.0–174.0 due to configurational sensitivity and thus used for microstructure determination. The expanded carbonyl region is shown in *Figure 1*. These multiplets have been assigned as mm (δ 172.0–172.6), mr(rm) (δ 172.6–172.87) and rr (δ 172.87–173.7) triads from high to low field. The area under these signals were calculated using the nonlinear curve fitting program. Using the triad concentration data, one can test whether the propagation reaction obeys Bernoullian statistics[2] by calculating the $P_{r/m}$ and $P_{m/r}$. When $P_{r/m} + P_{m/r} = 1$, then chain propagation obeys Bernoullian statistics. For PAB, the sum of the $P_{r/m}$ and $P_{m/r}$ equals 0.99, which approximate to 1 within experimental error, thus the polymerization obeys Bernoullian statistics. The triad concentrations calculated from the Bernoullian statistical model[2], using the average P_m value of 0.40 ± 0.01, are compared with those determined from n.m.r. spectroscopy and was found to have good agreement.

Table 1 $^{13}C\{^1H\}$n.m.r. experimental chemical shifts and relevant assignments for poly(*trans*-4-acryloyloxyazobenzene) P(AB)

Carbon atoms	Chemical shifts (ppm)[a]
C1	152.12
C2	122.16
C3	124.14
C4	150.45
C5	152.39
C6	122.91
C7	128.97
C8	130.97
C9	172.76
C10	41.0–42.8
C11	33.5–40.0

The ^{13}Cn.m.r. spectrum of the homopolymer have been completely assigned. The proton NMR spectrum of poly(*trans*-4-acryloyloxyazobenzene) is shown in *Figure 3*. To assign the complex proton spectrum of the homo polymer, $^1H - ^{13}C$ shift correlation (HSQC) spectrum was recorded and is shown in *Figure 4a* and *b*. In *Figure 4b*, the methine and methylene proton shows cross-peaks with corresponding methine and methylene carbons at δ 3.13 and 2.62–2.0 , respectively. The methyl protons of the AIBN shows cross peak at δ 1.46 . The aromatic methine protons region show three multiplets. These multiplets have been assigned with the help of 2D HSQC spectrum (*Figure 4a*). The signal at δ 7.24 is assigned to H2 methine proton. The methine protons H3 and H6 signals are at δ 7.84 and δ 7.80. The broad signal around δ 7.4–7.5 is assigned to H7 (δ 7.41) and H8(δ 7.44). This can be clearly seen in the DQF COSY spectrum (*Figure 5a*) of the poly(*trans*-4-acryloyloxyazobenzene) homopolymer. In *Figure 5a*, the cross-peak at δ 7.24/7.84 is assigned to the H2/H3 methine protons couplings. Similarly, the cross-peak at δ 7.41/7.80 is due to H6/H7 methine protons couplings. All the resonance signals

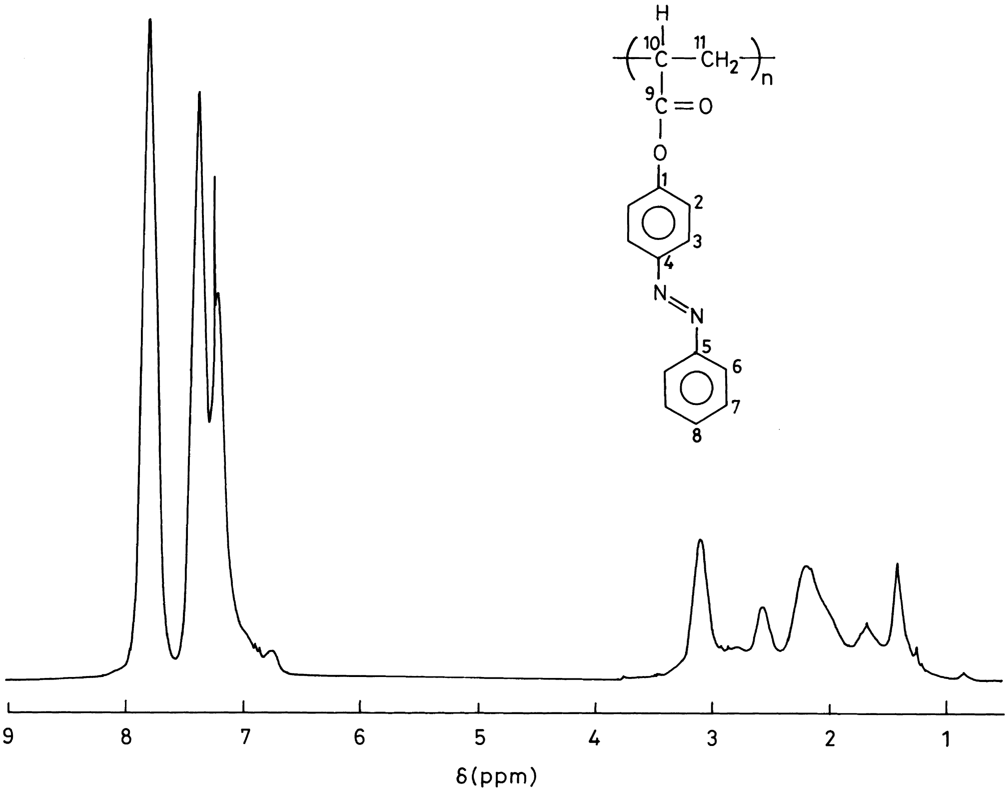

Figure 3 ^{1}Hn.m.r. spectrum of P(AB) recorded in CDCl$_3$ at 25°C

in the complex proton spectrum have been assigned without any ambiguity.

The various conformational assignment can be made with the help of 2D COSY and TOCSY experiment. In the 2D TOCSY experiment, depending on the mixing time, direct and indirect (long range relay coupling through magnetization transfer) couplings are seen. At shorter mixing time only direct couplings are seen. The cross-peaks observed in the 2D COSY spectrum are all the 1,3 interaction possible between the protons. In the meso dyad, the central methylene protons are non equivalent whereas the racemic dyad, due to symmetrical structure, will have equivalent methylene protons. Therefore, the cross-peaks at δ 35.75/2.59 and δ 35.75/2.00 in the inverse HETCOR spectrum (*Figure 4*b) are due to methylene protons of the meso dyad. In the aliphatic region of the COSY spectrum (*Figure 5b*) the cross-peaks at δ 3.13/2.59 and δ 3.07/2.00 are due to the coupling between the methine proton with the non equivalent methylene proton in the meso dyad. The geminal coupling between the two non-equivalent methylene protons is at δ 2.59/2.00 . The cross-peak at δ 3.13/2.21 is due to methine–methylene coupling in the racemic dyad. The four bond coupling, through magnetization transfer, between the methylene protons of racemic dyad and the non equivalent methylene protons of the meso dyad are at δ 2.21/2.59 and δ 2.0012.21 , respectively, in the 30 ms TOCSY spectrum (*Figure 6b*). The methyl proton of the AIBN initiator at δ 1.72 shows a three bond coupling with methylene proton at δ 2.32 . This

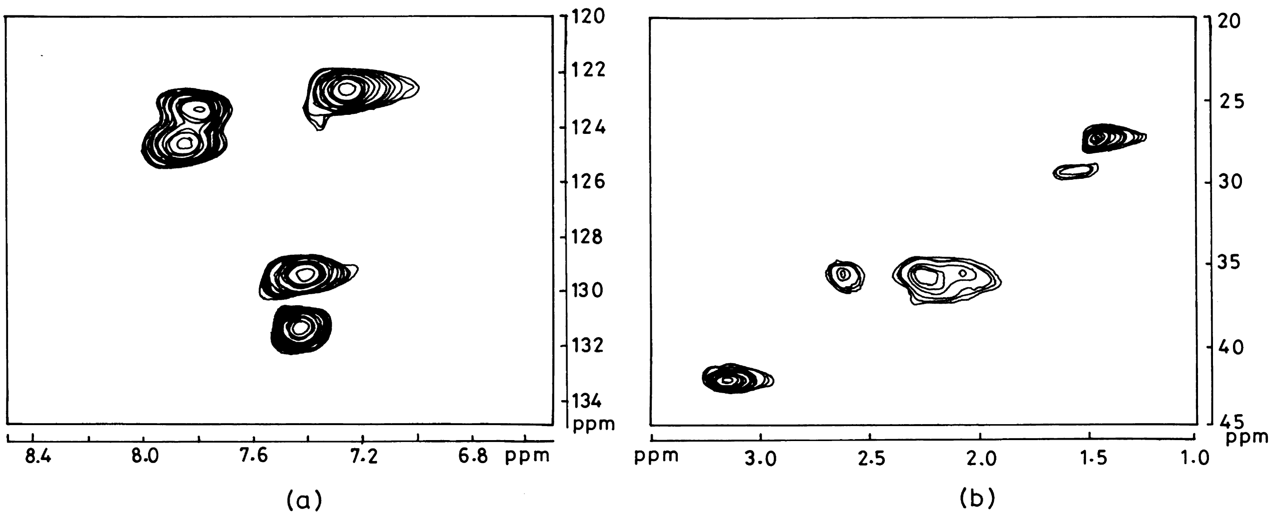

Figure 4 Heteronuclear single quantum correlation ^{13}C – ^{1}Hn.m.r. spectrum of: (a) aromatic; and (b) aliphatic regions of P(AB) recorded in CDCl$_3$ at 25°C

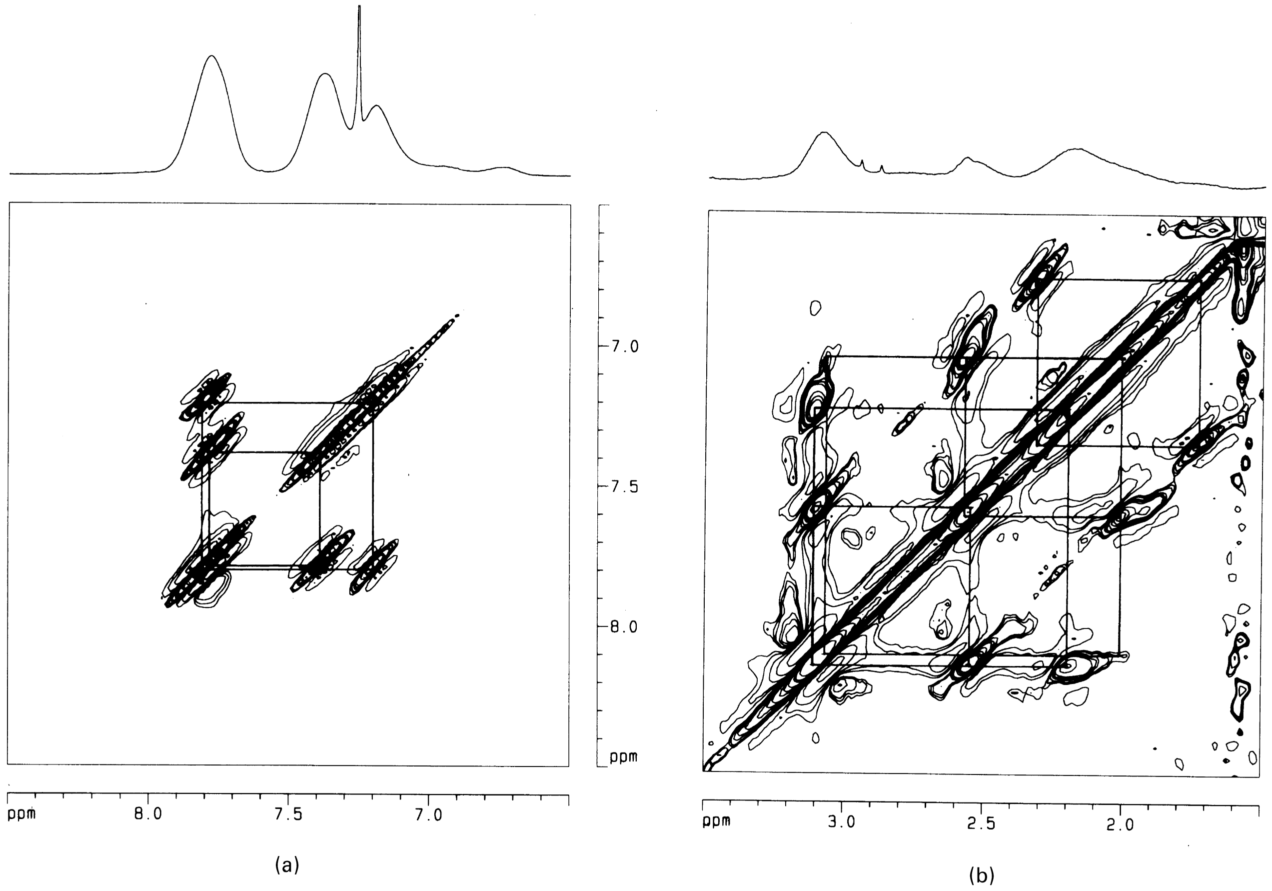

Figure 5 300 MHz 2D $^1H-^1H$ DQF COSY expanded spectrum of P(AB) recorded in $CDCl_3$: (a) aromatic; and (b) aliphatic regions

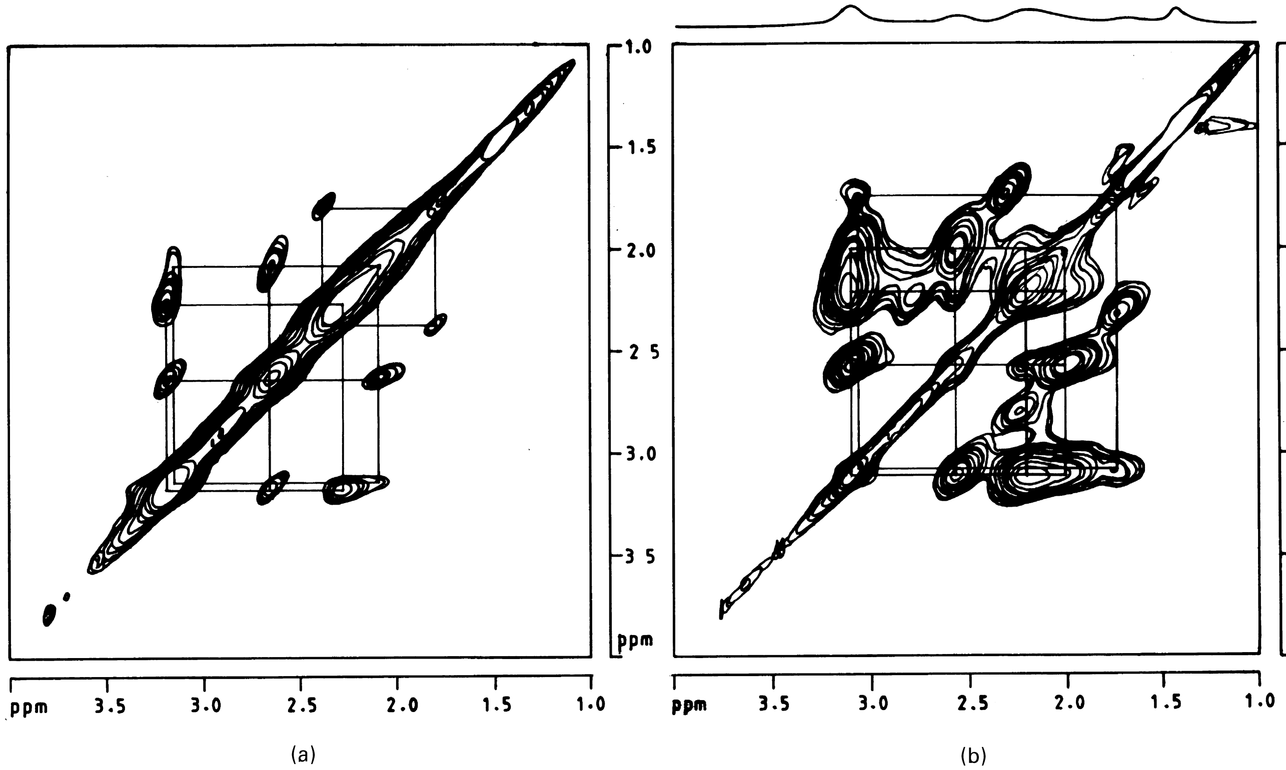

Figure 6 300 MHz 2D TOCSY spectrum at: (a) 4 ms and (b) 30 ms mixing time of P(AB) recorded in $CDCl_3$

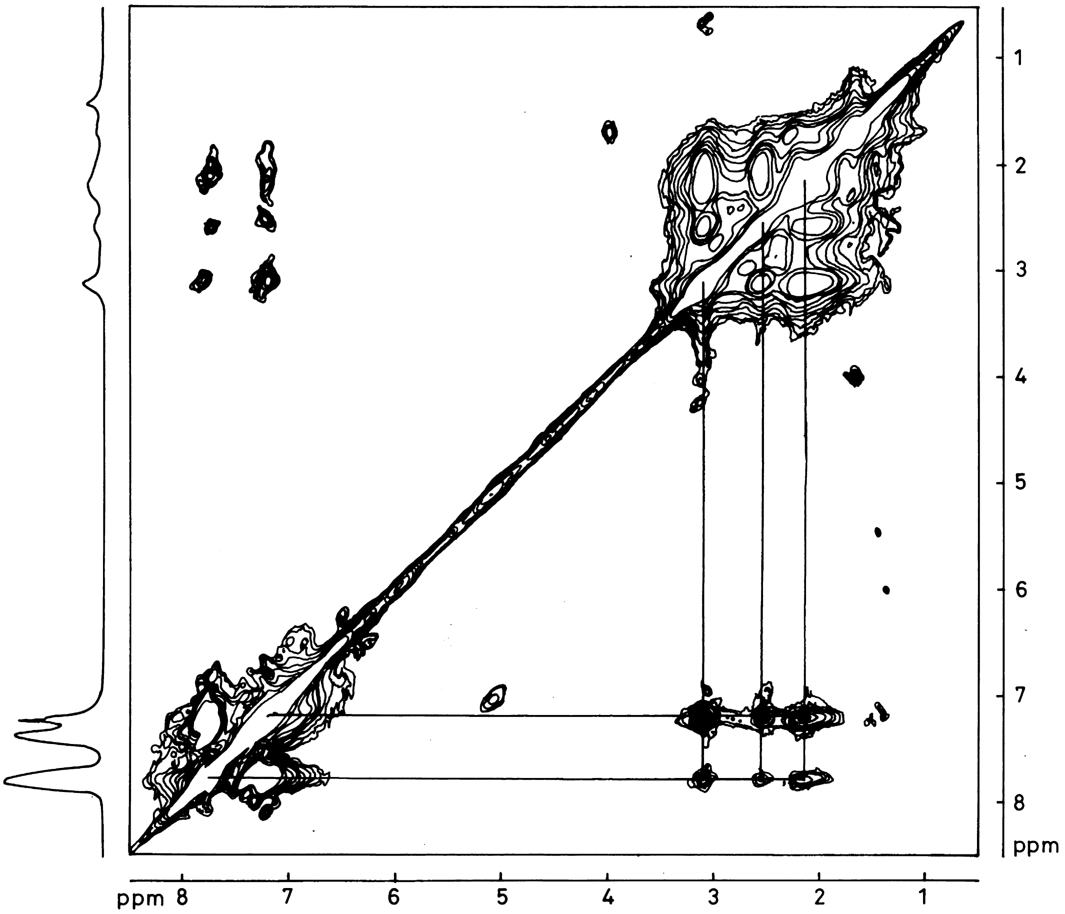

Figure 7 300 MHz 2D NOESY spectrum of P(AB) recorded in $CDCl_3$ at room temperature

methine proton also shows a three bond relay coupling with another methine proton at δ 3.13 ppm (*Figure 6b*).

Figure 7 shows the 2D NOESY spectrum of the poly(*trans*-4-acryloyloxyazobenzene) homopolymer. The mixing time of 350 ms was found to be optimum as there is no spin diffusion. In the NOESY spectrum there are cross-peaks due to the spatial coupling between the side-chain protons and the polymer backbone. The H2 and H3 methine proton show spatial coupling with the main methine and methylene protons. The spatial coupling between the other side-chain methine protons (H6, H7 and H8) and the main-chain methine and methylene are not seen. There is no NOE cross-peak between the methine protons of the two different benzene rings, which suggest that both the rings are in *trans* position to each other.

CONCLUSION

The stereochemical structure of poly(*trans*-4-acryloyloxyazobenzene) P(AB) was analysed by 1D and 2D n.m.r. spectroscopy. The resonance signals of methylene and methine carbons were distinguished using the DEPT n.m.r. spectroscopy. The heteronuclear $^1H-^{13}C$ 2D n.m.r. spectrum of the homopolymer was used for unambiguous assignment of the proton spectrum. The homonuclear 2D($^1H-^1H$) COSY and TOCSY spectrum suggested various configurational arrangements of the polymer chain. The microstructure of the poly(*trans*-4-acryloyloxyazobenzene) homopolymer was determined from $^{13}C\{^1H\}$n.m.r. spectroscopy. There was good agreement between the experimentally determined and theoretically calculated triad fractions. The homopolymerization mechanism obeyed Bernoullian statistic.

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