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NMR STUDIES ON SIDE CHAIN MESOMORPHIC POLYMERS

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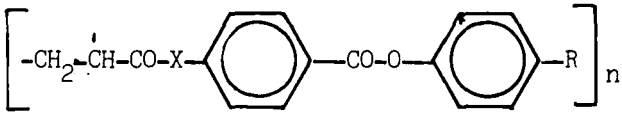
Abstract Nine polymers with general formula of



were investigated by high resolution ^{1}H and ^{13}C NMR spectroscopy in solution. The absorption lines were assigned. It was concluded from the line broadening that the mobility of the atoms in the main chain decreased when the aromatic cores were bonded to the main chain without spacer, but did not depend on the length of the spacer. The atomic mobilities increase with the distance from the main chain.
Two polymers with hexyloxy spacer were investigated by high resolution ^{13}C-NMR spectroscopy in bulk. The ring-current effect of aromatic carbon atoms in mesomorphic bulk before the isotropisation indicates rather a lamin ar structure than a nematic one.
The polymers with hexyloxy spacers contain $-CH_2COOCH_2-$ segments in the main chain resulted two extra lines in ^{1}H-NMR spectra. The appearence of these segments is based on a destructive chain transfer reaction. Thus, the polymers are rather copolymers than homopolymers.

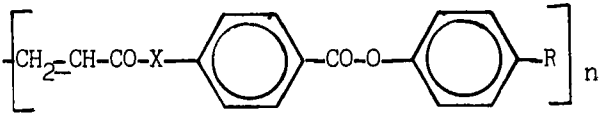
Keywords high resolution NMR, mesomorphic polymers, NMR spectra in bulk, ring-current effect, destructive chain transfer

INTRODUCTION

One of the authors[1] presented a thermodynamic model of the side chain mesogenic polymers. According to this model, the

properties of these polymers depend on the interaction of three parts of the polymers, i.e. the main chain, the rigid core and the soft segments of the side chains. The last part is either a spacer connecting the rigid core to the main chain or an alkyl chain at para position on the hard core. The present work aimed at studying the effect of these components on the dynamic behaviour of the polymeric system. NMR technique was chosen as an adequate method for investigating the selective mobilities of the atoms within a polymeric molecule[2-6]. It was interesting to compare the atomic mobilities in a dilute solution to those in the bulk or in the solid state[7]. Since a comprehensive study of the mobilities would be rather tiresome, the investigation of the effect of the different components on the mobilities was disregarded, only a homologous series of an acrylate polymer was investigated either in solution or in mesomorphic and in isotropic bulk state.

The polymers studied have a general formula of



where R= -H, $-OCH_3$ and $-O/CH_2/_3CH_3$, and X= -O-, $-O-CH_2CH_2-O-$ and $-O-/CH_2/_6-O-$. The abbrevation of the polymers are given in Table I.

TABLE I. The abbrevation of the polymers.

X = R =	-H	$-OCH_3$	$-O-/CH_2/_6CH_3$
-O-	PAB	MPAB	BPAB
$-O-CH_2CH_2-O-$	PAEB	MPAEB	BPAEB
$-O-/CH_2/_6-O-$	PAHB	MPAHB	BPAHB

This series of polymers has already been investigated by several methods[8-12]. All the polymers form mesomorphic structures. The polymers with X= -O- are very rigid. They have aperiodic helical geometry[8] /T_f 180 °C/. The others form unidentified lamellar structures. The polymers with spacers and with R= -/CH_2/$_3CH_3$ form S_C structures according to our miscibility studies[10,11].

EXPERIMENTAL

The syntheses of monomers and polymers are given in[8,9,12].

^{1}H-NMR studies were carried out in 12-15 mg/dm^3 deuterochlorophormic solution at room temperature by a JEOL GX-500 spectrometer at 500 MHz.

^{13}C-NMR studies were performed in 58-220 mg/dm^3 deuterochlorophormic solution at room temperature by a JEOL FX-100 spectrometer at 25 MHz in complete decoupling mode. Off-resonance mode was used for some samples to make adequate assignations possible. Tetramethyl silane was used as internal standard for the dissolved samples. Some of the spectra were also recorded with a BRUKER SPECTROSPIN instrument at 20 MHZ /PAHB, MPAHB, BPAEB/. The ^{1}H-NMR spectra of these polymers were also recorded by this instrument at 250 MHz.

The ^{13}C resonance spectra of MPAHB and BPAHB in bulk were recorded by a VARIAN XL-200 spectrometer at different temperatures from the glassy to the isotropic liquid states. No internal standard were used. The other polymers have clearing temperature above the upper limit of the apparatus.

RESULTS AND DISCUSSION

The ^{1}H and ^{13}C chemical shifts are demonstrated in Table II and Table III respectively. Assignation of the lines are

also given using the atomic abbrevations given in Figure 1.

TABLE II. ^{1}H-NMR chemical shifts of the polymers.

atoms	PAB	MPAB	BPAB	PAEB	MPAEB	BPAEB	PAHB	MPAHB	BPAHB
MC-1	3.044 2.75	3.073 2.75	3.031 2.78	2.455 2.2	2.454 2.278	2.464 2.277	2.320	2.276	2.279
MC-2	2.525 2.169 1.96	2.510 2.168 1.96	2.518 2.169 1.9	1.964 1.62 1.5	1.961 1.65 1.499	1.974	1.98	1.899	1.905
AR1-2	7.057	6.959	6.920 6.938 6.945	6.867	6.942 6.991	6.814 6.843	6.916	6.875	6.877
AR1-3	8.029	8.004	8.001	8.011	8.001	8.000	8.095	8.052	8.048
AR2-2	7.178	7.117	7.098 7.111 7.116	7.048 7.085 7.100	7.066 7.048	6.971 6.985 7.048 7.088 7.149	7.169	7.048 7.063	7.011 7.028 7.046
AR2-3	7.257	6.752	6.752	7.167 7.181 7.195	6.810 6.825	6.799	7.246 7.234	6.875	6.853
AR2-4	7.257	-	-	7.362	-	-	7.366	-	-
SP-1	-	-	-	4.054	4.045	4.036	3.987	3.948	3.897
SP-2	-	-	-	4.322	4.317	4.315 4.474	4.068	4.068	4.054
SP-11	-	-	-	-	-	-	1.789	1.757	1.747
SP-21	-	-	-	-	-	-	1.657	1.602	1.600
SP-12	-	-	-	-	-	-	1.458	1.389 1.454	1.443
PS-1	-	3.738 3.812 3.826	3.879 3.958 3.971 3.984	-	3.721 3.751 3.771	3.765 3.853 3.968	-	3.745 3.763	3.922 3.909 3.897
PS-2	-	-	1.792 1.729	-	-	1.690 1.705 1.854	-	-	1.723 1.719
PS-3	-	-	1.464 1.472	-	-	1.417 1.432 1.461	-	-	1.472 1.457
PS-4			0.956 0.966 0.970 0.984			0.921 0.937 0.951			0.967 0.952 0.943 0.929
Excess	-	-	-	-	-	-	4.312 2.661	4.296 2.643	4.293 2.637

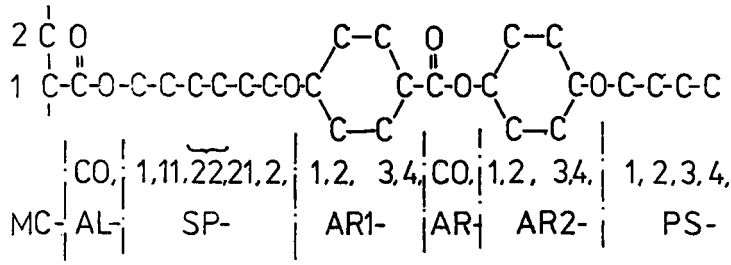


Figure 1. Atomic abbrevations used in Tables.

TABLE III. ^{13}C-NMR chemical shifts of the polymers.

atoms	PAB	MPAB	BPAB	PAEB	MPAEB	BPAEB	PAHB	MPAHB	BPAHB
MC-1	34.793	35.139	35.443 36.077 37.339	35.1	35	36		35.314	33.523 37.281
MC-2	41.919	41.860	41.771	41.273	41.242	41.619		40.831	40.773 41.449
AR1-1	153.990	153.906	153.906	162.388	162.360	162.332	163.415	163.178	163.149
AR1-2	127.721	127.754	127.782	114.307	114.355	114.279	114.357	114.133	114.133
AR1-3	131.713	131.654	131.657	132.183	132.155	132.155	132.147	132.099	132.099
AR1-4	121.587	121.559	121.559	121.648	122.409	122.352	121.682	121.704	121.794
AR2-1	150.618	144.075	143.958	150.853	144.748	144.132	150.246	144.797	144.249
AR2-2	121.587	122.352	122.320	122.320	122.409	122.352	121.998	122.409	122.352
AR2-3	129.337	114.301	114.894	129.337	114.335	114.922	129.287	114.368	114.955
AR2-4	125.842	157.137	156.780	125.669	157.109	156.696	125.535	157.072	156.696
AL-CO	172.280	172.290	172.252	174.130	174.189	174.159	175	174.046	174.039
AR-CO	163.826	164.154	164.211	164.446	164.793	164.793	164.609	165.000	165.028
SP-1	-	-	-	62.526	62.554	62.672	64.643	64.668	64.669 66.812
SP-2	-	-	-	65.725	65.726	65.755	68.175	68.015	68.015
SP-11	-	-	-	-	-	-	28.507	28.583	28.533
SP-22	-	-	-	-	-	-	25.666	25.685	25.744
SP-21	-	-	-	-	-	-	29.008	29.175	29.032
PS-1	-	55.422	67.986		55.481	67.986		55.509	68.015
PS-2	-	-	31.354	-	-	31.322	-	-	31.322
PS-3	-	-	19.357	-	-	19.198	-	-	19.227
PS-4	-	-	13.855	-	-	13.826	-	-	13.826
EXCESS							170.	170.198	170.166
								54.1 59.8	55.33 60.11

The spectra of polymers with X= -O- and -O-CH_2CH_2-O- are clearly resolved and assigned. The half width of the lines /see Figures 2 and 3/ indicates an increasing atomic mobility with their increasing distances from the main chain. The main chain is rigid when X= -O- in a good accordance with the prediction given in[1] and Tsuchihashi et al.[2] The main chain is less rigid when a spacer is present between the main chain and the hard core /Figure 3/ but its rigidity does not decrease with the increased length of the spacer. The atoms in the p-position of the hard core are very mobile

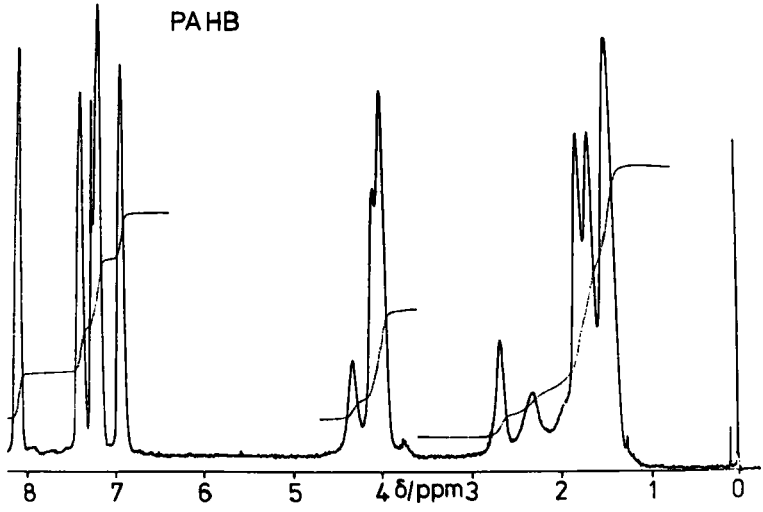


Figure 2. 250 MHz ^{1}H-NMR spectrum of poly/phenyl-p-acryloyl-oxy-hexyloxy-benzoate/ in deuterochlorophormic solution.

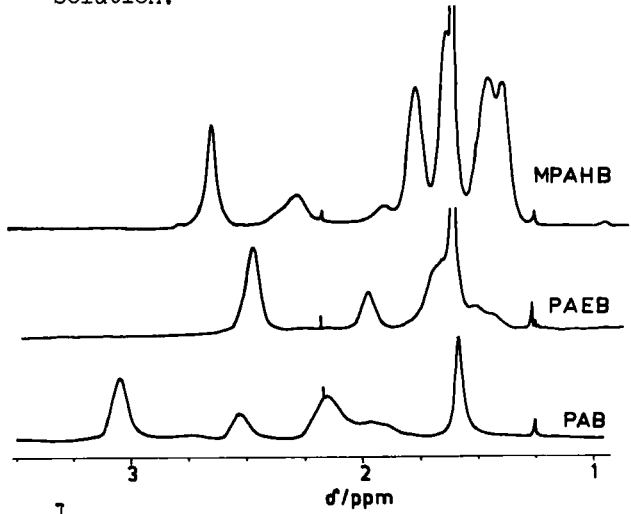


Figure 3. ^{1}H-NMR spectra of the protons in the main chain without spacers and with different length of the spacers of the polymers.

An increase in the atomic mobility with their increasing distance from the main chain was also reported in[5] and in.[6] The chemical shifts in the side chains are practically not sensitive to the presence or to the length of the spacer. The spacer influences only the chemical shifts of the main chain. These shifts can be explained readily by the effect of the presence of aromatic rings shifting the lines to higher frequencies /^{1}H spectra/. The ^{13}C chemical shifts of the main chain are not affected by the spacers. The values are near to those given in.[13]

There are two extra lines in the ^{1}H-NMR spectra of polymers with X= -O-/CH_2/$_6$-O-. One is at δ= 4.296 to 4.312 ppm, the other one is at = 2.637 to 2.661 ppm. The two lines have equal integral intensities but this value is different for the three polymers /1.0, 1.3 and 0.83 protons for PAHB, MPAHB and BPAHB, resp./.

There are extra lines in the ^{13}C-NMR spectra of same polymers, too. The lines at δ= 170 ppm indicate the presence of an aliphatic carbonyl group. The two other lines /appeare at BPAHB only/ are originated from alkyl carbon atoms beside -O- and -CO- atoms. According to P. Sohár[14], the extra lines may be attributed to a segment of R-CH_2COOCH_2-R' included into the main chain /the lines are not so sharp as those of the side chain atoms/. The phenomenon may be explained by a destructive chain transfer reaction to the first atom of the hexyloxy spacer at the carboxyl group. The remaining part of the side chain /pentyloxy and aromatic groups/ remaine in the solution after precipitation of the polymers. The fact that non-acrylate segments are inserted among acrylate anes in a ratio of 1 to 2 into the main chain involves that the polymer is a copolymer of the original monomer with a βoxy-propionate monomer.

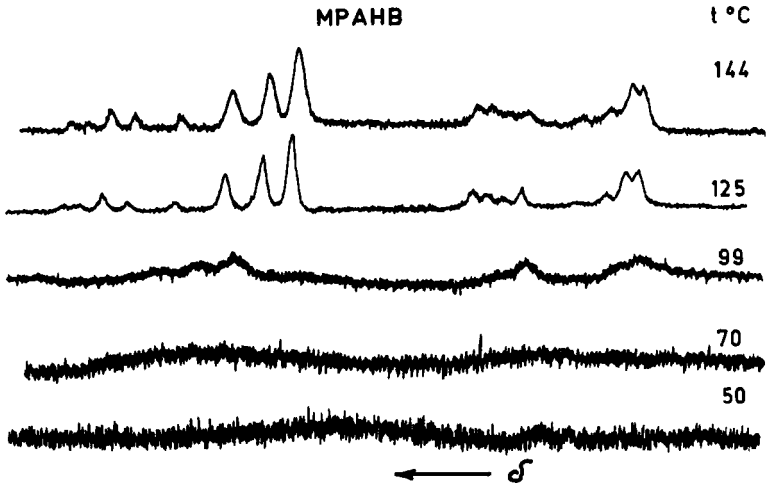


Figure 4. ^{13}C-NMR spectra of poly/p-methoxyphenyl-P-acryloyl oxy-hexyloxy-benzoate/ at different temperatures.

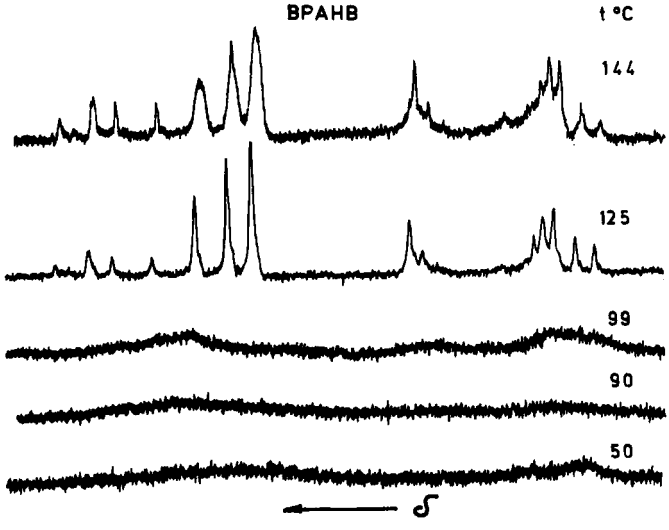


Figure 5. ^{13}C-NMR spectra of poly/p-butyloxyphenyl-p-acryloyloxy-hexyloxy-benzoate/ at different temperatures.

^{13}C bulk NMR spectra of MPAHB and BPAHB are given in Figures 4 and 5,resp. The resonance lines of the aliphatic, aromatic and the carbonyl groups are clearly visible in the isotropic states /125 and 144°C/. At lower temperatures, the resonance lines broaden and those of the aromatic carbon atoms are shifted to higher frequencies. Upon further cooling, the lines are very broad, mobilities freeze according to the high resolution NMR investigations.

The measurements were carried out in two steps. In the first cycle, the spectra were recorded at 50, 99 and 125°C. The other spectra were obtained in an other cycle after the samples had been cooled then kept at room temperature.

The shifts in the resonance lines at lower temperatures with respect to the greater ones indicate a ring-current effect. This means that the aromatic carbon atoms in the anisotropic state are in a close contact with other aromatic atoms. The same is valid in the layered smectic states. In the nematic state, the aromatic segments are mixed with aliphatic ones and a ring-current effect may not be observed. The layered structures are in good accordance with the miscibility studies of BPAHB[11].

A slight change in the chemical shifts upon solidifying to the opposite direction was reported by Jelinski et al.[7] at p-butylen-terephtalate and its copolymers. In this polymer, the closest packing in the crystalline state can be achived when the aromatic rings are in closed among butyloxy segments which explaines the ring-current effect with an opposite signe.

CONCLUSION

NMR studies permitted qualitativ detection of the increasing

atomic mobility with the increasing distance from the rigid main chain as discussed before[5,6].

The mobility of the atoms of the main chain in solution does not change with increasing length of the spacer from C_2 to C_6 while the glass transition temperature decreases. This means that vitrifying of the polymer is a macroscopic property, i.e. the plasticizing effect of the soft segments in the side chain[1] is affected by free volume created by the packing of the side chains.

The ring-current effect obtained in mesomorphic bulk with respect to the isotropic ones indicates rather a smectic than a nematic structure.

The presence of excess lines both in the ^{1}H and ^{13}C-NMR spectra of polymers with hexyloxy spacer indicates that these substances are copolymers with $-CH_2COOCH_2-$ segments in the main chain. The incorporation of these segments into the main chain is restricted by a destructive chain transfer reaction. Thus, the formerly drawn structural conclusions for acrylic or methacrylic polymers with longer spacers can be accepted only with precautions.

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