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4. ^{13}C-NMR Relaxation Study of Copolymers from 7-Oxabicyclo[2.2.1]heptane*

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Summary: Structure of copolymers obtained by ring opening cationic polymerization from 7-oxabicyclo[2.2.1]heptane and ethylene oxide has been recently reported. This study about the spin lattice relaxation times and Nuclear Overhauser enhancement factor in the carbon-13 NMR spectra was performed and the results interpreted in terms of different internal mobility of the units in the copolymer chain.

Introduction

Recently studies on the structure of copolymers obtained from 7-oxabicyclo[2.2.1]heptane (I) and ethylene oxide (II) by cationic ring opening polymerization have been reported (PACI et al. 1980):

(I)

(II)

On the basis of ^{1}H NMR and ^{13}C NMR spectra the microstructure has been elucidated and the results can be summarized as follows:

a) the repeating unit of (I) in the copolymer chain has a TRANS configuration,
b) the compositional sequences in the copolymer are generally statistical distributed, with a tendency toward alternation

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* Previous papers in this series are: G.CECCARELLI, F.ANDRUZZI, Makromol.Chem.180, 1371(1979); F.ANDRUZZI, G.CECCARELLI, M.PACI Polymer 21, 1180(1980); and ref (M.PACI et al. 1981).

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for high concentration of (I) in the feed.
With the aim to increase our knowledge on these copolymers, a carbon-13 NMR study of relaxation parameters, spin lattice relaxation time, T_1, and Nuclear Overhauser enhancement factor, NOEF, has been performed. The experimental results were interpreted in terms of different conformational mobility of the compositional triads.

Experimental

Mixtures of (I) and (II) were polymerized and the obtained copolymers were purified as described previously.
Copolymer samples with a molecular weight ranging from 8000 to 10000 were examined.
Carbon-13 NMR measurements were performed with a Bruker WH-90 at 22.63 MHz. FIDs were collected on 16K of memory and then FT transformed. Exponential filtering and automatic dynamic range reduction was avoided. Spin lattice relaxation times were measured with the $180°-\tau-90°$ pulse sequence waiting a time of 20 sec and accumulating for 500 scans. T_1 was evaluated with an exponential regression analysis and as a mean of three independent measurements. Protons were fully decoupled. NOEFs were measured with the gated decoupling technique and then evaluated from the integrated intensities of the individual resonances and those obtained with full proton decoupling. Temperature was keeped constant over all the experiments. Samples were solutions in CD_2Cl_2 20% w/v.

Results and Discussion

The carbon-13 NMR spectrum of the copolymer obtained using (I):(II)=1:1 is reported in Fig.1 with the assignment of the carbon atoms in the different compositional triads (M.PACI et al 1981).
The T_1 relaxation time and the NOEF values are reported in Table I. The same values were observed,within the experimental error(±10%), for the copolymers obtained with (I):(II) molar ratios in the feed: 0.7:0.3,1.0:1.0 and 0.3:0.7, respectively. T_1 and NOEF differences found denote that the carbon atoms of the copolymer units are sensitive to the mobility of the neighbouring units in the compositional triad.
The theory of carbon-13 NMR relaxation has been recently reviewed with respect the motions in synthetic polymer dilute solutions (F. HEATLEY 1979). The magnitude of T_1 and NOEF values depends on the frequency at wich C-H bonds are reoriented with respect to the laboratory frame, provided the relaxation occurs via a dipolar mechanism involving directly bonded protons.
T_1 relaxation time is given by (F.HEATLEY 1979):

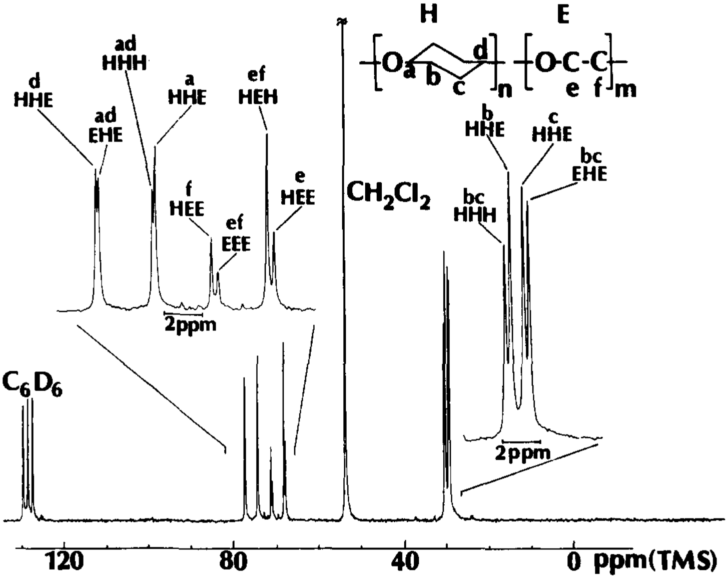

Fig.1: 22.63 MHz ^{13}C NMR spectrum of the copolymer obtained from an equimolar feed of (I) and (II). Ppm are from TMS. Assignments are reported in the inset.

TABLE I.

^{13}C NMR chemical shifts, relative assignment, T_1 spin lattice relaxation times and NOEF measured, T_1 and NOEF calculated and the related τ_o and τ_D values. Ppm are from internal TMS, assignments are referred to Fig.1.

δppm	Assign-ment	T_1 sec	NOEF	T_1 calc. sec	NOEF calc.	τ_o nsec	τ_D nsec
77.60	d HHE	0.517	1.67	0.516	1.70	1.58	7.4
77.40	a,d EHE	0.685	1.80	0.680	1.72	"	4.3
74.60	a,d HHH	0.592	1.27	0.590	1.71	10.	4.0
74.47	a HHE	0.535	1.55	0.535	1.71	1.58	6.9
71.45	f HEE	0.517	1.77	0.515	1.77	"	1.9
71.10	e,f EEE	0.731	2.0	0.730	1.87	"	1.0
68.50	e,f HEH	0.408	1.60	0.407	1.72	"	2.9
68.10	e HEE	0.537	1.62	0.537	1.72	"	1.7
30.90	b,c HHH	0.384	1.10	0.380	1.20	10.	4.7
30.60	b HHE	0.362	1.60	0.360	1.72	1.58	3.0
29.85	c HHE	0.500	1.64	0.500	1.72	"	1.9
29.60	b,c EHE	0.411	1.58	0.410	1.72	"	2.9

$$1/T_1 = 1/20\ (KN/r^6_{CH})\ \varphi \qquad (1)$$

where $\varphi = T(\omega_1)+T(\omega_2)+T(\omega_3)$ and $K = \gamma_H^2\ \gamma_C^2\ \hbar^2$,

$\omega_1 = \omega_H - \omega_C$, $\omega_2 = \omega_C$, $\omega_3 = \omega_H + \omega_C$, with the usual meaning.

Similarly the NOEF:

$$\mathrm{NOEF} = (\gamma_H/\gamma_C)\ (6T(\omega_3)-T(\omega_1))/\varphi . \qquad (2)$$

For a single isotropic correlation time τ the $T(\omega_n)$ has the familiar form:

$$T(\omega_n) = \tau(1+ \omega_n^2\ \tau^2)^{-1} \qquad (3)$$

A more realistic model must take into account the cooperative nature of segmental reorientation in polymers (B.VALEUR et al. 1975, F.HEATLEY et al. 1976, F.HEATLEY, 1979). The spectral density term $T(\omega_n)$ becomes:

$$T(\omega_n) = \tau_o\ \tau_D((\tau_o-\tau_D)^2+ \omega_n^2\ \tau_o^2\ \tau_D^2)^{-1}((\tau_o/2\ \tau_D)^{1/2}$$

$$((1+ \omega_n^2\ \tau_o^2)^{1/2}+1/(1+ \omega_n^2\ \tau_o^2))^{1/2}+ (\tau_o/2\ \tau_D)^{1/2}\ \omega_n\ \tau_o\ \tau_D . \qquad (4)$$

$$(\tau_o - \tau_D)\ ((1+ \omega_n^2\ \tau_o^2)^{1/2}-1/1+ \omega_n^2\ \tau_o^2)^{1/2}\ -1)$$

where τ_o characterizes the large scale tumbling motions and τ_D the local conformational jump motions. In our case the vicinal protons contribution to the relaxation was considered at a distance of 2.16 Å.
The comparison between the experimental and calculated values was made directly assuming that the overall tumbling correlation time τ_o must be the same for all the compositional triads in the copolymer. T_1 and NOEF calculated values are also reported in Table I with the τ_o and τ_D.
One can observe that the τ_o correlation time for the large scale overall tumbling motion does not differ in the different carbon atoms with the exception of those in the HHH triad (see Fig.1). The τ_o correlation time of the methine and methylene carbons of the central unit of this triad has a value of 10 nsec. All the other triads give for the central H carbon atoms a value of 1.58 nsec.
From the relationship : $\tau_{HHH}^{-1} = \tau_o^{-1} + \tau_{um}^{-1}$ (5)
a value of 1.92 nsec can be derived for the correlation time τ_{um} of an unknown motion (um). However it must be noted that this motion is present in all the E containing triads while it is missing only in the HHH triad. It appears reasonable to attribute the absence of this motion to the strong reduction in flexibility

of the ether bridge due to the intense steric interaction between the methine and methylene protons in the HHH triad.

The conformational jump correlation time τ_D reflects the mobility along the carbon-carbon bonds within the units of the copolymer chain.

The methine carbons of the H unit show different τ_D depending on the vicinity accross the ether bond of either an H or an E unit in the triad and on the presence of a second H or E unit in the triad.

The values indicate a faster motion for the methine of the EHE triad than those of the HHE and EHH ones.

The methylene carbons of the H unit in the HHH triad has the longest τ_D correlation time most probably due to the steric hindrance involved in the conformational transition of the cyclohexane ring in this triad.

In the triads other than HHH, the methylene carbons of the H unit have shorter correlation times than the methine carbons and very similar each other, so indicating a very fast conformational motion of the cyclohexane ring quite independent on the neighbouring units.

The methylene carbons of the E unit in the copolymer chain have a very short τ_D correlation time due to the very high mobility of this unit with respect to the conformational changes. Nevertheless a dependence can be pointed out on the presence of H units in the triad. In these cases the motion is slower than in the EEE triad. The presence of two H units, as in the HEH case, further decrease the mobility of these methylene carbons.

In conclusion a very different mobility has been pointed out for the individual carbons of the units of the copolymer from 7-oxabicyclo[2.2.1] heptane and ethylene oxide. The different environment in the compositional triads reflects in the conformational mobility in addition to the chemical shift as previously reported (M. PACI et al. 1980, M. PACI et al.1981). In general the presence of the E unit in the chain increases the flexibility of the copolymer.

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