Polymer Vol. 36 No. 17, pp. 3409–3411, 1995

0032-3861/95/$10.00+0.00

Entangled network formation in concentrated solutions of 1,2-polybutadiene by ^{13}C n.m.r. relaxation study

Shizhen Mao*, Shaoru Ni, Youru Du and Lianfang Shen
Laboratory of Magnetic Resonance and Atomic and Molecular Physics, The Chinese Academy of Sciences, Wuhan 430071, China
(Received 9 November 1994; revised 9 February 1995)

^{13}C n.m.r. relaxation studies can provide information about the exact location of an entanglement at the molecular level. The number of entanglements in the main chain is obviously larger than in the side chain. It is independent of the content of the 1,2-segment in polybutadiene, and of the kind of solvent.

(Keywords: relaxation; entanglement; polybutadiene)

Introduction

Entanglement and disentanglement are reversible dynamic processes which take place above the glass transition temperature T_g. In highly concentrated solutions of polymers, the entanglement behaviour is conventionally believed to be associated with factors such as molecular weight, concentration of the solution, and temperature. The molecular motions of polymers are largely dependent on the equilibrium between these factors. Pulsed n.m.r. techniques, especially the ^{13}C relaxation method, have been widely used to study the molecular motion of polymers. The spin–lattice relaxation times (T_1) of polymers, primarily related to the local environment of the nuclei, are sensitive to the high frequency motions in large regions of polymers, while the spin–spin relaxations (T_2) are sensitive to the slower relative translational motion and the low frequency motion of a polymer chain. It can provide information over longer ranges and about the microdimensions of small regions in polymers. However, much attention has been paid to relaxation time (T_1 and T_2) measurements rather than to the relaxation processes. Charlesby and Jaroszkiewicz studied entanglement in bulk polystyrene by ^1H spin–spin n.m.r. relaxation measurements[1]. Cohen-Addad and co-workers studied the property of temporary elasticity from the relaxation of the transverse magnetization of protons attached to high-molecular-weight polybutadiene chains in concentrated solutions[2,3] and the entanglement of *cis*-1,4-polybutadiene in concentrated solutions by observing the spectrum narrowing effects induced by sample rotation in proton spectra[4]. Owing to the low resolution of their methods and the limited information obtainable by T_2 measurements, they did not give the exact entanglement behaviour of individual carbon atoms in a molecular chain. Spin–lattice relaxation more directly reflects motions of segments in a molecular chain and thus contains more information about entanglement. The aim of this work is to study the entanglement properties of 1,2-polybutadiene (PB) by ^{13}C n.m.r. spin–lattice relaxation.

Results and discussion

The parameters of four 1,2-PB samples containing various amounts of 1,2-segments are listed in *Table 1*. In order to obtain better resolution of spectra and solvent dependence of entanglements, four PB samples with 7, 36, 49 and 71% of 1,2-segments were dissolved in toluene, deuterated benzene, deuterated chloroform and deuterated *ortho*-dichlorobenzene, respectively, to make 25 wt% solutions, which were degassed before measurement. ^{13}C spin–lattice relaxation curves of $-CH_2-$ in 1,4-chain segments and $-CH_2-$, $-CH$, $-CH=$ and $=CH_2$ in 1,2-chain segments of PB were obtained on a Varian XL-200 NMR spectrometer by the inverse recovery method. A pulse period longer than $5T_{1\max}$, probe temperature of 22–24°C, ^{13}C resonance frequency of 50.3 MHz and accumulation of data of 60–100 were used. The relaxation curves of these carbon nuclei show a typical two-exponential characteristic, i.e. they satisfy the relations:

$$\frac{M(t)}{M(\infty)} = 1 - 2\left[P_l \exp\left(-\frac{t}{T_{1l}}\right) + P_s \exp\left(-\frac{t}{T_{1s}}\right)\right] \quad (1)$$

$$P_l + P_s = 1 \quad (2)$$

where $M(\infty)$ and $M(t)$ are the magnetizations at time $t = \infty$ and t, and T_{1l} and T_{1s} are the long and short relaxation times of spin–lattice relaxations, respectively. The short and long relaxations correspond to the motion of entangled and free chain segments, respectively, in polymer chains, therefore P_s and P_l stand for their relative contents. The authors have studied the solvent effect of 1,2-PB by ^{13}C spin–lattice relaxation, where the spin–lattice relaxation process was assumed to be a single exponential[5]. After carefully checking the experimental relaxation process, by fitting the curves using equations (1) and (2), we found that there still exists a short relaxation fraction in the process, even though the long relaxation (T_{1l}) dominates. The values of T_{1s}, T_{1l}, P_s and P_l obtained from ^{13}C spin–lattice relaxation curves of 1,2-PB samples are listed in *Tables 2* and *3*. Generally, when the spin–lattice relaxation of a given ^{13}C nucleus in the polymer chain exhibits biexponential behaviour,

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* To whom correspondence should be addressed

these two different states of the nucleus are considered to be in two different phases of the bulk polymers. However, 25 wt% polymer solution should be homogeneous. As we have shown by nuclear Overhauser effect measurement[5], dipolar interaction dominates in this relaxation process. The short relaxation can be attributed to the intermolecular heteronucleus, i.e. ^{13}C and ^{1}H atoms of different molecules, dipole–dipole relaxation. Since the relaxation is proportional to the distance between the two nuclei, a, and their mutual self-diffusion coefficients, D, and inversely proportional to the concentration of the proton, N_H, the shorter the T_{1DD}, the smaller the D, the shorter the a and the larger the N_H. This is just the case for the two carbon atoms (attached by protons) of different molecular chains coming very close together, i.e. entanglement. Therefore, the fast relaxing nuclei should be attributed to those which are abnormally closely compacted in the system. This situation can only be understood by the existence of entanglements in the polymer system. The results in *Tables 2* and *3* show that about 20% of a given carbon atom in the main chain is involved in short relaxations, which means that as much as 20% of the carbon atoms are in the entanglement state. Because entanglement occurs between a pair of nuclei, this result implies that there is one entanglement point in every ten given carbon atoms in our case. This deviates a lot from the result in ref. 6, in which one topological entanglement point in every 150 chain units was reported. This difference is the experimental evidence for the existence of large amounts of entanglements other than the topological, namely cohesional entanglement[7]. This leads one to imagine that there should be bundles of the main chain segments distributed in the solution. *Table 2* also shows that

Table 1 The structural parameters of 1,2-polybutadiene

No.	L-3	D-4	V-61	L-6
cis-1,4-segment[a] (%)	41	32	24	16
trans-1,4-segment (%)	52	32	27	13
1,2-segment (%)	7	36	49	71
$[\eta]^b$, (dl g^{-1})	3.06	3.01	3.39	2.99

[a] Contents of chain segments measured by i.r.
[b] Data measured in toluene at 30°C

Table 2 The ^{13}C spin–lattice relaxation times of some carbon nuclei of 1,2-PB with different contents of 1,2-segments and in concentrated solutions of deuterated benzene

		L-3		D-4		V-61		L-6	
Groups		T_1 (s)	P(%)	T_1 (s)	P(%)	T_1 (s)	P(%)	T_1 (s)	P(%)
–CH=	slow	2.03	79	1.18	84	0.89	87	0.59	82
	fast	0.001	21	0.002	16	0.003	13	0.021	18
=CH$_2$	slow	0.77	97	0.51	94	0.37	94	0.25	91
	fast	0.024	3	0.002	6	0.002	6	0.001	9
$-\overset{|}{\mathrm{CH}}-$	slow	1.21	85	0.66	90	0.67	88		
(CVC)	fast	0.003	15	0.003	10	0.004	12		
–CH$_2$–	slow	0.96	83	0.61	83	0.61	82	0.49	76
(TTT)	fast	0.104	17	0.001	17	0.023	18	0.016	24
–CH$_2$–	slow	1.21	85	0.81	81	0.72	83		
(CCC)	fast	0.02	15	0.003	19	0.017	17		
–CH$_2$	slow	0.69	83	0.44	82	0.41	79	0.32	76
(CVC)	fast	0.029	17	0.004	18	0.002	21	0.07	24

Table 3 The ^{13}C spin–lattice relaxation times of some carbon nuclei of 1,2-PB (V-61) in concentrated solutions of different solvents

		$C_6H_5CH_3$		C_6D_6		$CDCl_3$		$C_6D_4Cl_2$	
Groups		T_1 (s)	P(%)	T_1 (s)	P(%)	T_1 (s)	P(%)	T_1 (s)	P(%)
–CH=	slow	0.95	78	0.89	87	1.12	84	0.69	88
	fast	0.015	22	0.003	13	0.024	16	0.031	12
=CH$_2$	slow	0.41	85	0.37	94	0.41	91	0.28	98
	fast	0.001	15	0.002	6	0.002	9	0.001	2
$-\overset{|}{\mathrm{CH}}-$	slow	0.70	89	0.67	88	0.81	84	0.50	84
(CVC)	fast	0.048	11	0.004	12	0.001	16	0.003	16
–CH$_2$–	slow	0.68	81	0.61	82	0.62	80	0.40	86
(TTT)	fast	0.025	19	0.023	18	0.015	20	0.029	14
–CH$_2$–	slow	0.97	78	0.72	83	0.84	79	0.48	83
(CCC)	fast	0.028	22	0.017	17	0.012	21	0.004	17
–CH$_2$–	slow	0.45	74	0.41	79	0.39	91	0.33	87
(CVC)	fast	0.02	26	0.002	21	0.035	9	0.083	13

entanglement behaviour is independent of the content of the 1,2-segment. Though collision probabilities between carbon nuclei are increased with increasing content of the 1,2-segment, the fraction with short relaxation is not increased as the 1,2-segment increases, because the side chains are so small that the distances between the carbon atoms in the 1,2-segments and other carbon atoms are much larger than the distance at which the strong interactions may occur. *Table 3* shows that the fraction (P_s) of entanglement network of PB is independent of the kind of solvent. The entanglement of the carbon atom on the end group of the side chain is very weak. This is evidence for faster free motion of the end groups than of the main chain[8]. The average lifetime of an entanglement point is very short, in the n.m.r. time scale, and cannot be observed by n.m.r. The carbon atom on the end group of the side chain behaves as slipping freely at the junctions. Consequently the ^{13}C n.m.r. relaxation study of polymers can provide information about the entanglement of individual carbon nuclei.

As stated above, the study of ^{13}C n.m.r. relaxation processes can provide information about the exact location of the topological and cohesional entanglement at a molecular level. The results show that about 20% of each of the carbon atoms in the main chain was entangled in the 25 wt% solution. It is independent of the 1,2-segment content in PB and of the kind of solvent. However, the entanglement of the carbon atom on the end group of the side chain is very weak and they behave as slipping freely at the junctions. A thorough and careful study of this is being made.

Acknowledgement

The authors thank Professor Renyaun Qian for his valuable suggestions.

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