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Microstructures of Poly(alkyl α-chloroacrylate) Determined by ^{13}C and ^{1}H NMR

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ABSTRACT: n-Butyl α-chloroacrylate (n-BCA), isobutyl α-chloroacrylate (i-BCA), *tert*-butyl α-chloroacrylate (t-BCA), n-hexyl α-chloroacrylate (n-HCA), cyclohexyl α-chloroacrylate (c-HCA), benzyl α-chloroacrylate (BzCA), and 2-chloroethyl acrylate (CECA) were polymerized by initiation with AIBN, γ-ray, and n-BuLi in toluene and THF. The microstructures were determined by ^{13}C NMR to give triad, tetrad, and pentad information from the carbonyl, backbone methylene, and quaternary carbon resonances, respectively. ^{1}H NMR spectra at 500 MHz were obtained for the first time for these polymers. The results of ^{13}C and ^{1}H NMR are in excellent agreement. Polymerizations initiated by AIBN, γ-ray, and n-BuLi in THF obey simple Bernoullian statistics, giving syndiotactic-rich products. Polymers obtained with n-BuLi in toluene are moderately isotactic. The P_r value, which is the probability for r placement, increases with bulkiness and polarity of the alkyl group.

Introduction

Alkyl α-chloroacrylates have been polymerized by free radical processes to find the percentage of head-to-head placements[1-3] and stereoregularity;[4,5] the alkyl groups are short in these studies (C_1–C_4). Recently, certain derivatives of α-chloroacrylates were found to display good sensitivity in electron beam lithography.[6-11] To eluidate the contribution of ester groups in radiolysis susceptibility, we have synthesized a number of poly(alkyl α-chloroacrylates), where R = n-butyl (P-n-BCA), isobutyl (P-i-BCA), *tert*-butyl (P-t-BCA), n-hexyl (PHCA), cyclohexyl (P-c-HCA), benzyl (PBzCA), and 2-chloroethyl (PCECA). The central purpose of this study is to determine the microstructures of these polymers to lay the groundwork for a subsequent study of the effect of the microstructures and the alkyl group on the radiolysis processes.

Experimental Section

Materials. The alcohols purchased from BDH were fractionally distilled. Quinoline from the same source was vacuum distilled prior to use. Methyl acrylate and *tert*-butyl acrylate from BDH and Fluka, respectively, were used as received. AIBN was recrystallized from methanol. n-Butyllithium as a 15% solution in n-hexane from Merck was used as received. Toluene and THF were dried according to standard procedure.[12,13]

Synthesis of Alkyl α-Chloroacrylates. Methyl and *tert*-butyl α-chloroacrylates were synthesized as follows:

$$\mathrm{CH_2{=}CHCOOR} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{Cl_2}} \mathrm{CH_2ClCHClCOOR} \xrightarrow[\text{quinoline}]{-\mathrm{HCl}} \mathrm{CH_2{=}CClCOOR}$$

$$\mathrm{R} = \mathrm{CH_3};\ \mathrm{C(CH_3)_3}$$

The other monomers are synthesized as follows:

$$\mathrm{CH_2{=}CHCOOCH_3} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{Cl_2}} \mathrm{CH_2ClCHClCOOCH_3} \xrightarrow[\text{reflux}]{20\%\ \mathrm{HCl}} \mathrm{CH_2ClCHClCOOH} \xrightarrow{\mathrm{SOCl_2}} \mathrm{CH_2ClCHClCOCl} \xrightarrow[-\mathrm{HCl}]{\mathrm{ROH}} \mathrm{CH_2ClCHClCOOR} \xrightarrow[\text{quinoline}]{-\mathrm{HCl}} \mathrm{CH_2{=}CClCOOR}$$

$$\mathrm{R} = \mathrm{CH_2CH_2CH_2CH_3};\ \mathrm{C_6H_{11}};\ \mathrm{CH_2CH(CH_3)_2};\ \mathrm{CH_2C_6H_5};\ \mathrm{C(CH_3)_3};\ \mathrm{CH_2CH_2Cl}$$

In the latter scheme, methyl acrylate was chlorinated to methyl 2,3-dichloropropionate (MDP), hydrolyzed to 2,3-dichloropropionic acid (DCPA), converted to 2,3-dichloropropionyl chloride (DCPC) by $\mathrm{SOCl_2}$, esterified to produce alkyl 2,3-dichloropropionate (RDCP) and finally dehydrochlorinated to the corresponding RCA. The conditions for these reactions are detailed below.

Methyl 2,3-Dichloropropionate. Methyl acrylate (500 mL) was placed in a 2-L three-necked flask fitted with a thermometer, inlet tube, and gas trap. Methanol (250 mL) was added and the solution was agitated with a magnetic stirrer. The flask was then immersed in an ice bath, and chlorine was passed into the ester over a period of 4 h, keeping the temperature below 40 °C. Methanol was distilled off, and MDP, a colorless liquid, was collected by vacuum distillation. Yield of the product was 750 g (86%), and the boiling point was 92–93 °C (48 mmHg).

2,3-Dichloropropionic Acid. With a similar apparatus as above, 175 g of MDP was mixed with 500 mL of 20% HCl in methanol and gently refluxed for 5 h. The mixture was cooled, filtered through glass wool, extracted with a large excess of chloroform, and dried over sodium sulfate. Chloroform and low-boiling products were removed by distillation under reduced pressure. The yield of the crude DCPA was 95 g (65% of the theoretical amount). The IR spectrum of the product exhibited $\bar{\nu}_{\mathrm{CO}}$ 1750, $\bar{\nu}_{\mathrm{COOH}}$ ~3000, and $\bar{\nu}_{\mathrm{CCl}}$ 720 cm^{-1}.[14]

2,3-Dichloropropionyl Chloride. To 95 g of DPCA in a 500-mL round-bottom flask was added dropwise 150 g of thionyl chloride. The reaction mixture was stirred overnight and then refluxed for 1–2 h. Excess of thionyl chloride was removed by distillation. The product DCPC was collected under reduced pressure with 83% yield, bp 52–54 °C (16 mmHg).

Alkyl 2,3-Dichloropropionates. DCPC (0.1 mol) was added to a 250-mL round-bottom flask containing 0.15 mol of dry alcohol. The mixture was heated to 100 °C for about 15 min. The ester was then distilled under vacuum. The IR spectra of RDCP has absorptions at 1760 and 710 cm^{-1} showing the presence of ester and chlorine.

Alkyl α-Chloroacrylates. In a 250-mL three necked flask was introduced 0.1 mol of RDCP, followed by 20 min of purge with dry nitrogen, and 0.11 mol of quinoline was added slowly as the mixture turned reddish brown. At this point, the mixture was heated gently and a dark reddish brown material precipitated, which is, presumably the quinoline hydrochloride. The RCA, a colorless liquid, was immediately distilled from the reaction mixture under reduced pressure. Data regarding boiling point, yield and elemental analysis for all the monomers are listed in Table I.

Polymerization. Free Radical. AIBN was used to initiate radical addition polymerization of RCA monomers at 55 °C.[15]

Anionic. A two-necked flask, fitted with rubber septum and vacuum stopcock, was flamed for 15 min under vacuum. The flask

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Table I
Physical Properties and Elemental Analysis of Alkyl α-Chloroacrylates

alkyl group	yield, %	bp, °C (torr)	density, g/mL	% C calcd	% C expt	% H calcd	% H expt
methyl	65	65–68 (48)	1.189 ± 0.001	39.83	39.79	4.11	4.18
hexyl	69	86–88 (7)	1.020 ± 0.002	56.69	56.64	7.89	8.63
cyclohexyl	62	90–94 (8)	1.057 ± 0.001	57.29	56.99	6.90	7.18
benzyl	62	120–123 (8)	1.030 ± 0.009	61.07	61.47	4.58	5.15
2-chloroethyl	59	84–86 (7)	1.234 ± 0.002	35.50	35.81	3.55	4.47
n-butyl	61	92–93 (20)	1.050 ± 0.000	51.69	52.35	6.79	7.02
isobutyl	61	91–92 (25)	1.030 ± 0.001	51.69	52.03	6.79	7.39
tert-butyl	58	74–76 (35)	1.011 ± 0.005	51.69	49.77	6.79	6.94

was sealed and transferred into a glovebag under nitrogen atmosphere. The appropriate amount of *n*-butyllithium was added into the flask through the rubber septum. The flask was then taken out of the glovebag and cooled to −84 °C. The solvent (toluene or THF) was charged into the flask, and while the solution was stirred with a magnetic bar the RCA was introduced. The reaction was continued at −84 °C for 4 h and then was brought to room temperature and quenched with 10% methanolic HCl. The polymer was filtered and purified by dissolving and precipitating in chloroform and methanol, respectively. The polymer was dried under vacuum at 40 °C.

γ-Irradiation. Requisite amounts of RCA monomer and solvent were charged into a glass tube and subjected to vacuum–freeze–thaw cycles, and then the tube was sealed. The sealed tubes were irradiated with a ^{60}Co source to 0.2–0.5-Mrad dose. After polymerization, the product was poured into methanol. The polymers were purified and dried as described before.

IR. Infrared spectra were recorded with a Perkin-Elmer spectrophotometer.

NMR. Proton-noise-decoupled ^{13}C NMR spectra were obtained on a 15–20 wt % solution in $CDCl_3$. The instrument used was JEOL–JNM FX-100 FT NMR spectrophotometer operating at 25.05 MHz, with a pulse width of 4–6 μs (30° flip angle), 3-s pulse delay, 60–50 Hz spectral width, and 16K data points for Fourier transform.[16]

It has been observed by Schaefer and Natusch[17] for many synthetic polymers in solution that the NOE and spin–lattice relaxation time are similar for different types of carbons in or near the polymer main chain. Wehrili and Wirtilin[18] suggested that for macromolecules having molecular weight above 300 the NOE is complete for all carbon atom types, including the quaternary ones. The lower pulse flip angle and longer pulse delay time used in this work would allow the reestablishment of longitudinal magnetization to 99% of its equilibrium value. In such cases the relative peak areas are proportional to the number of contributing atoms.

Since our experimental conditions satsify the above requirements, the numbers of different carbon atoms are proportional to the relative peak areas. This was performed with the aid of computer read out as well as measurement of peak areas by cutting and weighing.[29] The data obtained by both methods were in good agreement.

It is fairly well documented that the spin–lattice relaxation time is longer for ^{13}C nuclei in isotactic sequences than those in syndiotactic sequences.[19–22] Hatada and co-workers[23,24] found a longer ^{13}C spin–lattice relaxation time for the *mmm* tetrad peak in isotactic poly(ethyl α-chloroacrylate) as compared to the *rrr* peak in the corresponding syndiotactic polymer, but no significant differences were seen for the spin–lattice relaxation times in the same polymer. Consequently, small differences in spin–lattice relaxation times were considered to be insignificant in the present investigation.

The instrument used for 500-MHz ^{1}H NMR spectra was a Bruker AM-30 NMR spectrophotometer. The spectra were recorded at 50 °C with $CDCl_3$ as solvent and Me_4Si as internal standard.

Results and Discussion

Polymerizations. Table II summarizes the experimental polymerization conditions and yields. In general the bulk polymerizations initiated by AIBN have higher yields than those in toluene solution. The rates of polymerization are in the order of *n*-HCA, c-HCA < BzCA, CECA < *n*-BCA, *i*-BCA, *t*-BCA. The rates of polymerization by γ-ray of all the monomers are about the same within a factor of 2; it decreases slightly with decreasing temperature. Anionic polymerization in THF produces syndiotactic-rich products closely resembling those by free radical initiation, indicating the propagating species to be free ions in this polar solvent. If nonpolar toluene is used for the same *n*-BuLi anionic initiator at the same temperature, the polymer is moderately isotactic, suggesting either an ion pair or solvent-separated ion pair as the propagating species.

Polymer Characterizations. Molecular Weights and Distribution. The number-average and weight-average molecular weights along with the molecular weight distribution for PRCA synthesized with AIBN in toluene are presented in Table III. The data reveal that the polymers are of high molecular weights. Since all the polymers were obtained under identical synthetic conditions, the data show the effect of alkyl group on the molecular weight. PHCA and PBzCA have higher molecular weights than the other homopolymers, which can be due to the steric effect of the bulky pendant groups on the rates of termination. PCECA and P-*i*-BCA have relatively low molecular weights, possibly due to side-chain transfer reactions. P-*t*-BCA has the lowest MW of this series; the *tert*-butyl group may cause a slow rate of propagation.

Elemental Analysis. The elemental analysis results of all the poly(alkyl α-chloroacrylates) synthesized in toluene are presented in Table IV. The good agreement between the experimental data and the calculated values showed that the polymers are pure and that lactonization reaction[25] did not occur under our experimental conditions.

Solubility. Poly(alkyl α-chloroacrylates) were soluble in common solvents like toluene, chloroform, tetrahydrofuran, dimethylformamide, and dimethylsulfoxide. The polymers were insoluble in nonpolar and hydroxy solvents like hexane, heptane, methanol, 2-propanol, and water. P-*t*-BCA was soluble in methanol.

Infrared Spectra. The infrared spectra of PHCA, P-c-HCA, and PBzCA are characterized by absorption peaks around 1740 and 730 cm^{-1} that were due to $\nu_{C=O}$ and ν_{CCl}, respectively. the aromatic $\nu_{C=C}$ of phenyl group at 1500 cm^{-1} in spectra of PBzCA showed the presence of benzyl groups in the polymers. The double carbonyl absorption for α-halo esters is an indication of rotational isomerization. Furthermore Dever et al.[4,5] reported that the two carbonyl absorptions at 1742 and 1772 cm^{-1} of poly(methyl α-chloroacrylate) correlated well with diad tacticity. The carbonyl double-resonance frequency appears to be sensitive to tacticity. The quantitative microtacticity data could not, however, be obtained because of insufficient changes in relative absorption peaks at 1760 and 1742 cm^{-1}.

^{13}C NMR. Poly(cyclohexyl α-chloroacrylate). The ^{13}C NMR of P-c-HCA, synthesized with radical initiator

Table II
Reaction Conditions for the Synthesis of Poly(alkyl α-chloroacrylates)

polymer	initiator, %	solvent[a]	temp, °C	time, h	yield, %	tacticity[b]
P-*n*-BCA (1)	AIBN (0.1)		55	7	30	syn
P-*n*-BCA (2)	AIBN (0.1)	T	55	5	50	syn
P-*n*-BCA (3)	γ-ray		30	3	10	syn
P-*n*-BCA (4)	BuLi (1)	THF	−84	3	20	syn
P-*i*-BCA (1)	AIBN (0.1)		55	7	28	syn
P-*i*-BCA (2)	AIBN (0.1)	T	55	5	20	syn
P-*i*-BCA (3)	γ-ray		30	3	13	syn
P-*i*-BCA (4)	γ-ray		0	3.5	6	syn
P-*i*-BCA (5)	BuLi (1)	T	−84	3	4	mod iso
P-*i*-BCA (6)	BuLi (1)	THF	−84	3	2	syn
P-*t*-BCA (1)	AIBN (0.1)		55	5	32	syn
P-*t*-BCA (2)	AIBN (0.1)	T	55	5	46	syn
P-*t*-BCA (3)	γ-ray		0	2	7	syn
P-*t*-BCA (4)	γ-ray		30	2	5	syn
P-*t*-BCA (5)	γ-ray		−56	5	6	syn
P-*t*-BCA (6)	γ-ray	T	30	5	16	syn
P-*t*-BCA (7)	BuLi (1)	THF	−84	3	2	syn
PHCA (1)	AIBN (0.1)		55	5	20	syn
PHCA (2)	AIBN (0.1)	T	55	5	9	syn
PHCA (3)	AIBN (0.1)	THF	55	5	4	syn
PHCA (4)	γ-ray		0	2	9	syn
PHCA (5)	γ-ray		30	2	5	syn
PHCA (6)	γ-ray		−56	5	21	syn
PHCA (7)	γ-ray	T	30	5	10	syn
PHCA (8)	γ-ray	THF	30	5	7	syn
PHCA (9)	BuLi (1)	THF	−84	3	3	syn
P-c-HCA (1)	AIBN (0.1)		55	5	28	syn
P-c-HCA (2)	AIBN (0.1)	T	55	7	15	syn
P-c-HCA (3)	AIBN (0.1)	THF	55	7	9	syn
P-c-HCA (4)	γ-ray		0	2	10	syn
P-c-HCA (5)	γ-ray		30	2	12	syn
P-c-HCA (6)	γ-ray		−56	5	15	syn
P-c-HCA (7)	γ-ray	T	30	5	10	syn
P-c-HCA (8)	γ-ray	THF	30	5	15	syn
P-c-HCA (9)	BuLi (1)	THF	−84	3	4	syn
P-c-HCA (10)	BuLi (1)	T	−84	3	3	mod iso
PBzCA (1)	AIBN (0.1)		55	7	30	syn
PBzCA (2)	AIBN (0.1)	T	55	7	18	syn
PBzCA (3)	AIBN (0.1)	THF	55	7	11	syn
PBzCA (4)	γ-ray		30	3	11	syn
PBzCA (5)	BuLi (1)	THF	−84	3	8	syn
PBzCA (6)	BuLi (1)	T	−84	3	5	mod iso
PCECA (1)	AIBN (0.1)		55	7	25	syn
PCECA (2)	AIBN (0.1)	T	55	7	18	syn
PCECA (3)	AIBN (0.1)	THF	55	7	12	syn
PCECA (4)	γ-ray		30	2	13	syn

[a] T indicates toluene. [b] syn indicates syndiotactic rich; mod iso indicates moderately isotactic.

Table III
Molecular Weight and Molecular Weight Distribution of Poly(alkyl α-chloroacrylates)

alkyl group	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
n-butyl	1.43	2.32	1.62
isobutyl	1.27	2.97	2.34
tert-butyl	0.96	1.98	2.06
cyclohexyl	2.34	4.31	1.84
n-hexyl	2.16	2.92	1.35
2-chloroethyl	1.26	2.34	1.86
benzyl	2.46	4.95	2.01

Table IV
Elemental Analysis of Poly(alkyl α-chloroacrylates) Synthesized with Radical Initiator (AIBN) in Toluene

	% C		% H		% Cl	
alkyl group	calcd	found	calcd	found	calcd	found
hexyl	56.69	55.61	7.89	7.10	18.64	18.96
cyclohexyl	57.29	57.02	6.90	7.11	18.83	18.55
2-chloroethyl	35.50	35.87	3.55	3.76	42.01	40.36
benzyl	61.07	60.89	4.59	4.55	18.07	17.86
n-butyl	51.69	51.26	6.79	7.41	21.85	21.56
isobutyl	51.69	50.64	6.79	7.24	21.85	21.67
tert-butyl	51.69	51.82	6.79	7.01	21.85	21.78

is shown in Figure 1 with assignments given in the inserts of expanded spectra for the carbonyl, backbone methylene, and quaternary carbons. The backbone methylene ^{13}C NMR at ca. 50 ppm contains six peaks corresponding to six possible configurational tetrads. The most intense one at 55.01 ppm can be assigned to *rrr* because polymers synthesized with radical initiator are rich in syndiotactic structure. The last and the weakest peak was assigned as *mmm*. Elementary statistical principle gives the following relationship between the various tetrads:[26]

$$mmm + mmr + mrm + rmr + rrm + rrr = 1 \qquad (1)$$

$$mmr + 2(rmr) = mrr + 2(mrm) \qquad (2)$$

The second quality is an excellent test for the peak assignments since it is independent of any propagation model such as Bernoullian or Markovian. Thus any set of assignments that do not satisfy 2 must be incorrect;[26] this requirement is met reasonably well for the peak areas of the six tetrads of P-c-HCA. The resonances for the six tetrads are found in the order of increasing field strength as

$$rrr < rrm < rmr < mmr < mrm < mmm \qquad (3)$$

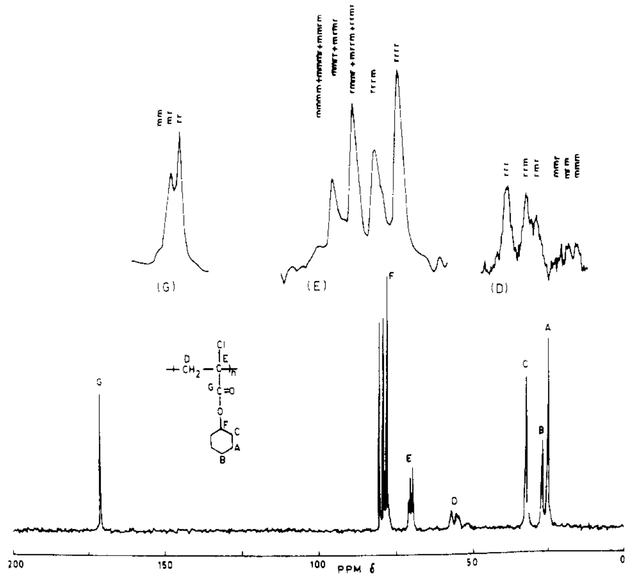

Figure 1. ^{13}C NMR spectrum of poly(cyclohexyl α-chloroacrylate) synthesized with AIBN in THF at 55 °C.

Table V
Tetrad Assignments for Backbone Methylene Carbon Resonance of Poly(cyclohexyl α-chloroacrylate)

assignt	chem shift, ppm	peak area, %	calcd for P_r = 0.73
mmm	49.42	5	1
mmr	51.70	10	11
mrm	50.15	6	5
rmr	52.70	13	14
rrm	53.61	28	29
rrr	55.01	37	39

Table VI
Triad Assignments for Carbonyl Carbon Resonance of Poly(cyclohexyl α-chloroacrylate)

assignt	chem shift, ppm	peak area, %	calcd for P_r = 0.73	calcd from tetrad
rr	168.20	54	53	51
mr	168.39	38	39	39
mm	168.63	8	7	10

Table V lists the tetrad assignments (column 1), chemical shifts (column 2), integral peak areas (column 3), and relative resonance intensities calculated according to the Bernoullian model (P_r = 0.73) (column 4). The values in the last two columns are in close agreement as expected for free radical polymerization of acrylates.

The carbonyl carbon resonance consists of three peaks at 168.63, 168.39, and 168.20 ppm, attributable to the *mm*, *mr*, and *rr* triads, respectively. The relative intensities of these three peaks agree well with the fractions calculated for Bernoullian statistics (P_r = 0.73) (Table VI). In addition, the triad tacticities calculated from experimental tetrad populations using the following relationships:

$$mr = {}^1/_2[mmr + 2(rmr) + mrr + 2(mrm)]$$

$$rr = rrr + {}^1/_2 rrm$$

$$mm = mmm + {}^1/_2 mmr \qquad (4)$$

are in good agreement (Table VI, column 5).

There are five quaternary carbon peaks around 68 ppm suggesting pentad splitting. However, they are insufficient to permit complete pentad assignments. The strongest peak at the highest field can be assigned to *rrrr* pentad.

Table VII
Pentad Assignments of Quaternary Carbon Resonance of Poly(cyclohexyl α-chloroacrylate)

assignt	chem shift, ppm	peak area, %	calcd for P_r = 0.73	
mmmm	69.15	4	–	6
mmmr			3	
mmrm			3	
mmrr	68.86	15	8	16
mrmr			8	
mrrm	68.45	28	4	29
rmmr			4	
rrm			21	
rrrm	68.02	19	21	
rrrr	67.55	33	28	

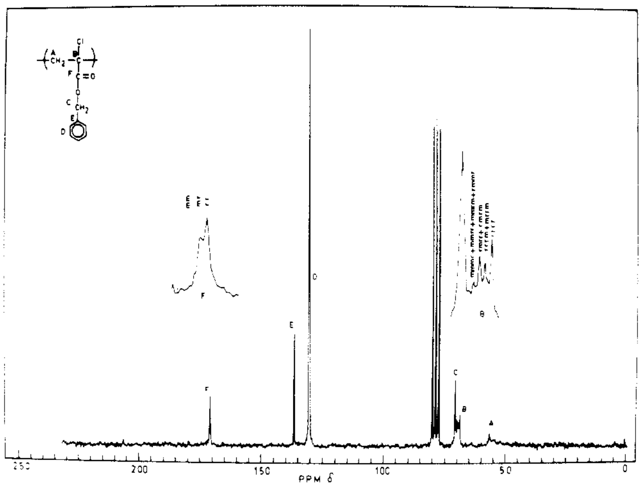

Figure 2. ^{13}C NMR spectrum of poly(benzyl α-chloroacrylate) obtained with AIBN initiation; "P" insert is for the expanded quaternary carbon region of PBzCA synthesized with *n*-BuLi in toluene at −84 °C.

Based on *rrrr* = 0.33, which was obtained from its peak intensity and corresponded to a propagation probability of P_r = 0.73, the remaining peaks were assigned (Table VII). The pentad tacticity values obtained from the quaternary carbon resonance are seen in good agreement with those calculated from Bernoullian statistics.

Analysis of the ^{13}C NMR spectra of P-c-HCA synthesized by γ-irradiation gave similar triad and pentad distribution from the carbonyl and quaternary carbon resonance data, respectively. The Bernoullian P_r value was 0.78. The results suggest that there is little difference in tacticity between the polymers obtained by γ-ray and AIBN initiations under our experimental conditions (Table I).

Poly(benzyl α-chloroacrylate). AIBN or γ-ray initiation produces PBzCA that has ^{13}C NMR (Figure 2) as described above for P-c-HCA: the peak intensities are in agreement with Bernoullian statistics for propagation (P_r = 0.75). The same is true for PBzCA polymerized by BuLi in THF.

Anionic polymerization of BzCA in nonpolar toluene gave PBzCA enriched in isotactic sequences, as can be seen in the "P" expanded region inset of Figure 2 for the quaternary carbon. There is an intense peak due to pentads originated from *mm* triads. Comparison of the spectra in this region for the two PBzCA in Table VIII showed the isotactic-rich polymer cannot be described by simple Bernoullian statistics. Similar solvent effects on tacticity have been reported for many methacrylates.[27,28] It has often been proposed that isotactic placement is favored for the ion pair propagating species. But the degree of dissociation of ion pairs is strongly dependent on solvent

Table VIII
Pentad Assignments for Quaternary Carbon Resonances of PBzCA Rich in Syndiotactic and Isotactic Microstructures

	syndiotactic[a]			isotactic[b]
assignt	peak area, %	calcd for $P_r = 0.73$		peak area, %
rrrr	26	28		17
rrrm	25	21	25	14
mrrm		4		
rmrr	29	21	29	24
rmrm		8		
mmrr	21	8	21	44
mmrm		3		
rmmr		4		
mmmr		3		
mmmm		1		

[a] Synthesized with *n*-butyllithium in THF at −84 °C. [b] Synthesized with *n*-butyllithium in toluene at −84 °C.

Table IX
Triad and Tetrad Assignments for Poly(*n*-butyl α-chloroacrylate)

assignt	chem shift, ppm	peak area, %	calcd for $P_r = 0.72$
Triad Assignments (Carbonyl Carbon Resonance)			
rr	168.69	49	52
mr	169.87	41	40
mm	169.17	10	8
Tetrad Assignments (Backbone Methylene Carbon Resonance)			
rrr	55.00	36	37
rrm	53.70	27	29
rmr	52.70	16	15
mrm	51.31	8	6
mmr	50.39	10	11
mmm	49.69	6	2

Table X
Triad and Pentad Assignments for Poly(isobutyl α-chloroacrylate)

assignt	chem shift, ppm	peak area, %	calcd for $P_r = 0.77$	
Triad Assignments (Carbonyl Carbon Resonance)				
rr	168.64	53	59	
mr	168.93	39	35	
mm	169.36	8	5	
Tetrad Assignments (Backbone Methylene Carbon Resonance)				
rrrr	67.05	35	35	
rrrm	67.47	20	21	
mrrm	67.96	24	3	24
rmrr			21	
rmrm	68.26	14	6	14
mmrr			6	
mmrm			2	
rmmr	68.57	5	3	5
mmmr			2	
mmmm	68.75	2	0	

Table XI
Pentad Assignments for Poly(*tert*-butyl α-chloroacrylate)

assignt	chem shift, ppm	peak area, %	calcd for $P_r = 0.83$	
rrrr	69.24	47	48	
rmrr	68.81	18	19	
mrrr	69.78	26	19	25
mrrm			2	
mrmr			4	
mmrr	70.82	9	4	8
mmrm			1	
rmmr			2	
mmmr			1	
mmmm			0	

polarity, temperature, and ionic size, which in turn determines the rate constant and stereospecificity of monomer insertion. These chemical dynamics cannot be simply approximated by two active species, i.e., free ions and contact ion pairs.

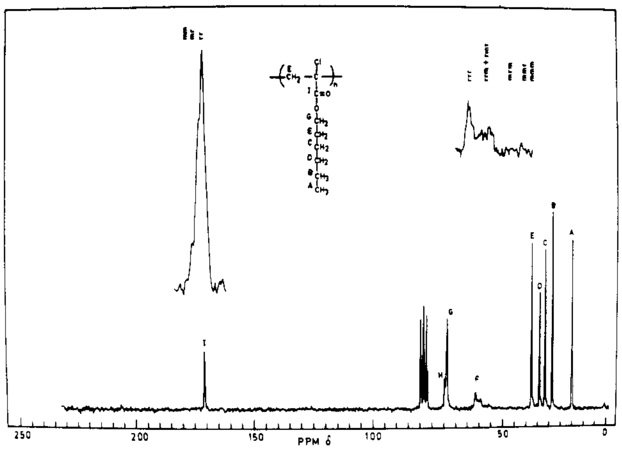

Figure 3. ^{13}C NMR spectrum of poly(isobutyl α-chloroacrylate) synthesized with AIBN in toluene at 55 °C.

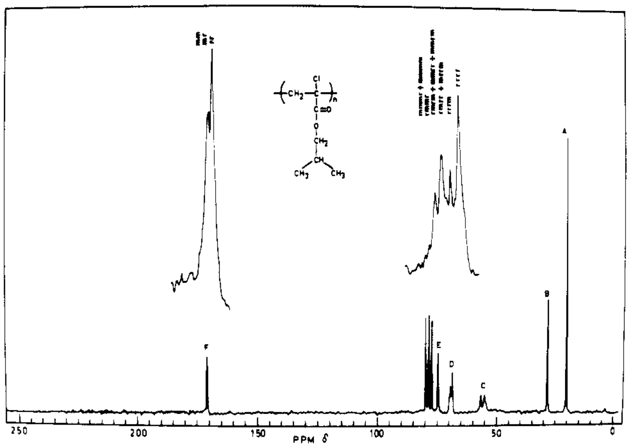

Figure 4. ^{13}C NMR spectrum of poly(2-chloroethyl α-chloroacrylate) synthesized with AIBN in toluene at 55 °C.

Table XII
Triad and Tetrad Assignments for Poly(*n*-hexyl α-chloroacrylate)

assignt	chem shift, ppm	peak area, %	calcd for $P_r = 0.73$	
Triad Assignments (Carbonyl Carbon Resonance)				
rr	168.63	52	53	
mr	168.81	38	39	
mm	169.17	10	8	
Tetrad Assignments (Backbone Methylene Carbon Resonance)				
rrr	55.13	39	39	
rrm	53.44	34	29	34
mrm			5	
rmr	50.76	17	12	
mmr	49.66	8	10	
mmm	49.08	2	2	

Table XIII
Pentad Assignments for Poly(2-chloroethyl α-chloroacrylate)

assignt	chem shift, ppm	peak area, %	calcd for $P_r = 0.76$	
rrrr	67.05	34	33	
rrrm	67.84	26	21	25
mrrm			4	
rmrr	67.41	28	21	28
rmrm			7	
mmrr	68.20	12	7	14
mmrm			2	
rmmr			3	
mmmr			2	
mmmm			0	

Table XIV
Chemical Shifts of Carbonyl and Quaternary Carbon Resonances in Poly(alkyl α-chloroacrylates)[a]

	chemical shift,[b] ppm		
	carbonyl		quaternary
alkyl group	*mm*	*rr*	*rrrr*
n-butyl	169.17	168.69	66.99
isobutyl	169.36	168.69	67.05
hexyl	169.17	168.63	67.05
cyclohexyl	168.81	168.20	67.60
benzyl	168.93	168.51	66.98
2-chloroethyl		167.54	67.05
tert-butyl		168.02	69.24

[a] In Me_2SO. [b] In $CDCl_3$ solvent and at 50 °C unless otherwise stated.

Table XV
Stereoregularity of Poly(alkyl α-chloroacrylates)[a]

	tacticity, %		
alkyl group	*rr*	*mr*	*mm*
n-butyl	49	41	10
isobutyl	53	39	8
tert-butyl	68	29	3
hexyl	52	38	10
cyclohexyl	54	38	8
benzyl	57	38	5
2-chloroethyl	58	36	6
methyl[b]	60	33	7
ethyl[b]	63	29	8

[a] Polymerization at 55 °C initiated by AIBN unless otherwise stated. [b] Polymerization at −50 °C initiated by photolysis of benzoyl peroxide. Reference 4.

Poly(alkyl α-chloroacrylates). The ^{13}C NMR spectra of P-*i*-BCA and PCECA synthesized by using radical initiator are shown in Figures 3 and 4. Spectra for P-*n*-BCA, P-*tBCA*, and PHCA have also been obtained but are not reproduced here to save space. The assignments of each carbon and agreement found for the observed microstructures and those calculated for Bernoullian statistics are given in Tables IX–XIII.

The alkyl ester group displays certain influence on chemical shifts of carbonyl and quaternary carbon resonances. In Table XIV, the chemical shifts of carbonyl carbon (*rr* and *mm*) and quaternary carbon (*rrrr*) for various PRCA are summarized. The quaternary carbon in *rrrr* pentad always resonates at a higher field than that of a *mmmm* pentad. This is in contradistinction to the carbonyl spectra of poly(alkyl methacrylates), which has the *rrrr* pentad located at lower fields than *mmmm* peaks.[29] Also, in PRCA the *rr* peaks are located at higher field than the *mm* peaks, while the opposite holds for poly(alkyl methacrylates) and for poly(alkyl α-bromoacrylates).[24] However, the reason for this effect is not known.

The triad tacticity data for poly(alkyl α-chloroacrylates) synthesized with radical initiation is summarized in Table XV. It is evident from the table that syndiotactic content increases with increase in polarity and bulkiness of the alkyl group. This is consonant with the lower activation energy requirement for a syndiotactic placement than an isotactic alteration because of the lesser degree of steric interaction that arises from the bulky side groups in the syndiotactic configuration as compared to the corresponding isotactic configuration. This difference is greater for more bulky substituents.

^1H NMR. The 500-MHz ^1H NMR spectra has been obtained for all the PRCA's; the spectra for P-c-HCA, P-*n*-BCA, and PHCA are shown in Figures 5–7, respectively. These spectra should give microstructural information consistent with those obtained above with ^{13}C NMR. We illustrate this with the analysis of the backbone methylene protons with those for the corresponding car-

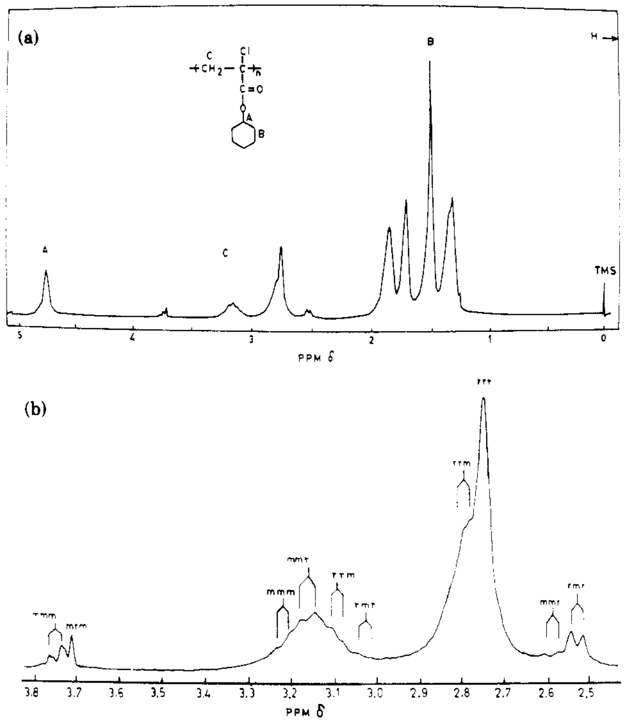

Figure 5. ^1H NMR spectrum of poly(cyclohexyl α-chloroacrylate): (a) full 500-MHz spectrum; (b) expanded backbone methylene proton region.

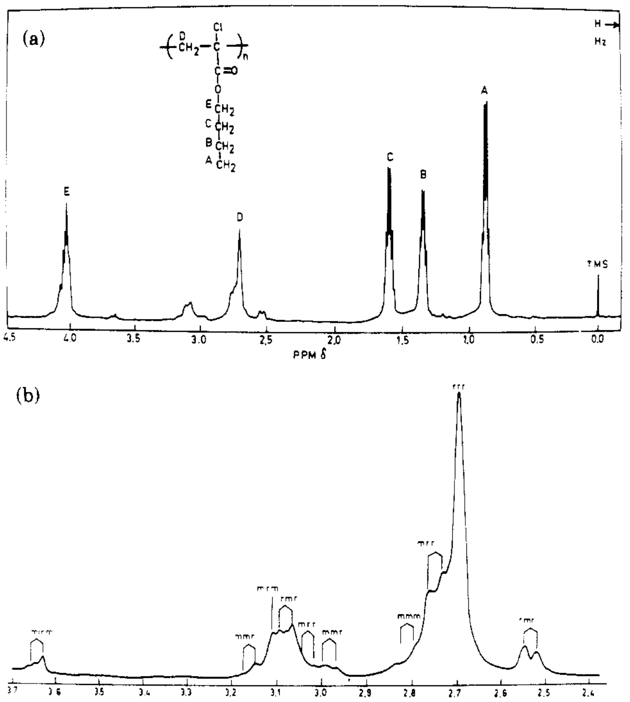

Figure 6. ^1H NMR spectrum of poly(*n*-butyl α-chloroacrylate): (a) full 500-MHz spectrum; (b) expanded backbone methylene proton region.

Table XVI
Tetrad Tacticity in Vinyl Polymers

tacticity	heterosteric tetrads	homosteric tetrads
isotactic	*mmm*	
heterotactic	*rmr*	*mrm*
atactic	*mmr*	
atactic	*mrr*	
syndiotactic		*rrr*

Table XVII
Tetrad Assignments for Poly(alkyl α-chloroacrylates) Using 500-MHz ^{1}H NMR

	P-c-HCA				P-*n*-BCA				P-*n*-HCA			
	chem shift, ppm		coupling constant,	rel peak	chem shift, ppm		coupling constant,	rel peak	chem shift, ppm		coupling constant,	rel peak
assignt	obsd	av	Hz	area, %	obsd	av	Hz	area, %	obsd	av	Hz	area, %
mmm	3.733, 3.244	3.489	14.6	5	3.545, 3.853	3.699	15.0	4	3.543, 2.835	3.189	15.0	4
mmr	3.149, 2.588	2.869	14.9	12	3.161, 2.980	3.071	15.0	6	3.133, 2.735	2.934	14.9	8
rmr	2.523, 3.028	2.776	14.9	12	2.534, 3.079	2.807	14.9	14	2.519, 3.041	2.780	14.1	13
mrm	3.701	3.701		3	3.018	3.018		6	3.087	3.087		6
mrr	2.815, 3.094	2.955	15.0	33	2.748, 3.030	2.899	14.6	31	2.735, 2.998	2.867	15.0	30
rrr	2.748	2.748		35	2.695	2.695		39	2.748	2.748		39

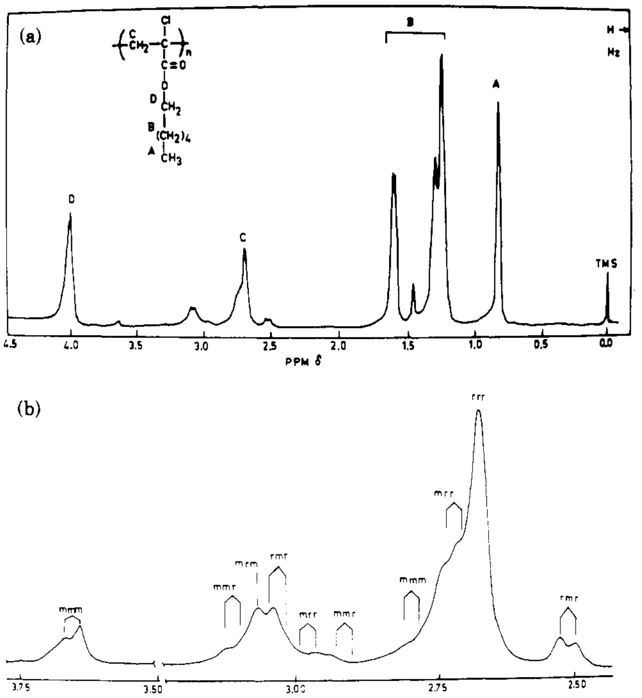

Figure 7. ^{1}H NMR spectrum of poly(*n*-hexyl α-chloroacrylate): (a) full 500-MHz spectrum; (b) expanded backbone methylene proton region.

bon. There should be a total of 18 tetrad peaks as defined in Table XVI,[5] which must obey the following conditions for internal consistency.[4,5,26] The chemical shifts of the *m*-centered tetrads should increase with field strength as *mmm* < *mmr* < *rmr*, while the order is *mrm* < *mrr* < *rrr* for the *r*-centered tetrads. The relative magnetic nonequivalence for the two heterosteric backbone methylene protons should have chemical shifts differences in the order *mmm* > *mmr* > *rmr* > *mrr*. The *m*- and *r*-centered tetrads are related by *mmr* + 2(*rmr*) = *mmr* + 2(*mrm*). Needles to say, the Bernoullian probabilities obtained from ^{1}H and ^{13}C NMR should be identical.

The ^{1}H NMR spectra were analyzed and the results for the tetrad structures are summarized in Table XVII and found to generally satisfy the above conditions with certain minor variations. For instance the tetrads in P-c-HCA are in the order *mrm* < *mmm* < *mrr* < *mmr* < *rmr* < *rrr*; it is *mmm* < *mmr* < *mrm* < *rrm* < *rmr* < *rrr* in P-*n*-BCA and *mmm* < *mrm* < *mmr* < *rrm* < *rmr* < *rrr* with increasing field in P-*n*-HCA. The distribution of tetrads by ^{1}H NMR showed that they can be described by Bernoullian statistics (Table XVIII) with the same P_r values derived from the ^{13}C NMR data as shown in Table XIX.

Table XVIII
Comparison of Tetrad Peak Intensities Observed in ^{1}H NMR with Calculations for Bernoullian Statistics

	P-c-HCA		P-*n*-BCA		P-*n*-HCA	
assignt	obsd	calcd for P_r = 0.73	obsd	calcd for P_r = 0.72	obsd	calcd for P_r = 0.73
mmm	5	1	4	2	4	2
mmr	12	11	6	11	8	10
mrm	3	5	6	6	13	12
rmr	12	14	14	15	6	5
rrm	33	28	31	29	30	29
rrr	35	39	39	37	39	39

Table XIX
Comparison of P_r Values Obtained from ^{13}C and ^{1}H NMR for Poly(alkyl α-chloroacrylates) Synthesized with AIBN

	rrr chem shift, 500-MHz NMR,	P_r	
alkyl group	ppm	^{1}H NMR	^{13}C NMR
n-butyl	2.695	0.73	0.72
isobutyl	2.700	0.73	0.77
tert-butyl	2.741	0.84	0.83
hexyl	2.680	0.74	0.73
cyclohexyl	2.741	0.73	0.73
benzyl	2.672	0.68	0.75
2-chloroethyl	2.805	0.74	0.76

Conclusions

The analysis of the configurational sequence statistics of polymers can provide information concerning the propagation mechanism. The simplest type of sequence statistics results from building a chain by Bernoullian trial where all the tactic sequences are generated by only one probability P_r (or $P_m = 1 - P_r$), where the monomer placement is completely independent of the stereochemistry of the propagating chain end. The configuration statistics of all the polymers synthesized with free radical initiators have been found to follow this propagation model. The polymer synthesized with γ-radiation have also been found to follow this model. The polymers synthesized with *n*-BuLi in toluene did not follow this model, but those synthesized in THF do follow this propagation statistics. Unfortunately, the moderately isotactic polymers synthetized by *n*-BuLi in toluene could not be tested for other models because of insufficient splitting. It may be noted that the other models can only be tested if triad or higher order splittings are observed.[29]

Acknowledgment. This work was supported in part by a grant from ONR.

Registry No. Poly(*n*-butyl α-chloroacrylate) (homopolymer), 80347-31-5; poly(isobutyl α-chloroacrylate) (homopolymer), 29756-03-4; poly(*tert*-butyl α-chloroacrylate) (homopolymer), 100655-48-9; poly(cyclohexyl α-chloroacrylate) (homopolymer), 31740-95-1; poly(*n*-hexyl α-chloroacrylate) (homopolymer), 100655-49-0; poly(2-chloroethyl α-chloroacrylate) (homopolymer), 29756-05-6; poly(benzyl α-chloroacrylate) (homopolymer), 100655-50-3; methyl α-chloroacrylate, 80-63-7; hexyl α-chloroacrylate, 13401-86-0; cyclohexyl α-chloroacrylate, 2177-72-2; benzyl α-chloroacrylate, 93856-55-4; 2-chloroethyl 2-chloroacrylate, 44806-25-9; *n*-butyl α-chloroacrylate, 13401-85-9; isobutyl α-chloroacrylate, 44901-96-4; *tert*-butyl α-chloroacrylate, 72088-85-8; methyl acrylate, 96-33-3; methyl 2,3-dichloropropionate, 3674-09-7;

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2,3-dichloropropionic acid, 565-64-0; 2,3-dichloropropionyl chloride, 7623-13-4.

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Magnetic Properties of Very Low and Very High Molecular Weight Polyacetylenes

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ABSTRACT: Magnetic properties of $[CH]_x$ with number-average molecular weight ($\bar{M}_n$) from 480 to 870 000 have been studied and compared with those with $\bar{M}_n \sim 11\,000$ prepared by the standard Ito–Shirakawa–Ikeda procedure. The very low $\bar{M}_n$ *cis*-$[CH]_x$ has a T_1 value of ca. 190 μs, which decreases with increasing molecular weight (MW). The values of T_1 of *trans*-$[CH]_x$ are also MW dependent, decreasing from 64 ± 22 μs to about 20 μs, but T_2 increases from 64 ± 22 ns to ca. 100 ns with increasing MW. The unpaired-spin concentrations $[S\cdot]$ for *cis*-$[CH]_x$ are quite variable from sample to sample for all MW. Upon heating, *cis*-$[CH]_x$ isomerizes to *trans*-$[CH]_x$ with a relatively constant $[S\cdot]_m$ of $(4.8 \pm 1.2) \times 10^{-4}$ spins/CH for all polymers. Iodine doping of *trans*-$[CH]_x$ has no effect on $[S\cdot]_m$ until $y(I_3^-) \sim 3 \times 10^{-4}$, above which $[S\cdot]$ decreases rapidly with increasing doping. In the case of *cis*-$[CH]_x$ light doping increases $[S\cdot]$, but the trend is reversed above $y \sim 3 \times 10^{-4}$. Iodine doping of *trans*-$[CH]_x$ decreases T_1 monotonically beginning at the ppm level of I_3^-, whereas T_2 remains constant until $y = (1\text{–}3) \times 10^{-4}$ before its value decreases. In contrast, for $0 < y < 1.7 \times 10^{-3}$, iodine-doped low MW *cis*-$[CH]_x$ has constant values of $T_1 = 187 \pm 54$ μs, $T_2 = 11.6 \pm 0.8$ ns, and $\Delta H_{pp} = 5.6 \pm 0.4$ G. The EPR cannot be saturated at higher dopant concentration. When EPR is observable, it has a Lorentzian line shape and a Curie temperature dependence. The above effects of doping are the same for polymers of different MW. These results are interpreted to mean interchain spin diffusion or hopping is the determinant for some aspects of spin dynamics.

Introduction

Polyacetylene can be synthesized with predominantly cis or trans structures.[1] The former can be thermally isomerized to the latter, which is the thermodynamically stable form.[2] Most *trans*-$[CH]_x$ specimens are prepared by this method instead of the alternate ones by high-temperature polymerization or doping or compensation. *trans*-$[CH]_x$ is said to be unstable toward a commensurate Peierls distortion (index of 2) to a bond-alternate semiconducting state.[3] The neutral topological defect is said to have soliton wavelike characteristics.[4] Many spectroscopic and transport properties have been interpreted as the manifestation of solitons.[5] Solitons cannot exist in *cis*-$[CH]_x$ because the neutral defect is confined in this polymer. Differences in the EPR of the unpaired spins in the two isomers were the first evidence cited for the existence of solitons.[6] The diffusion of a soliton should be one-dimensional. There have been various attempts to estimate the anisotropy through the analysis of EPR line shape, proton T_1, dynamic nuclear polarization, and spin-echo data. We have used the effect of dopant on EPR saturation[7] to obtain the diffusion coefficients in *trans*-$[CH]_x$: $D_\parallel = 3.8 \times 10^{14}\ s^{-1}$ and $D_\perp = 1.1 \times 10^9\ s^{-1}$. Therefore, there is a nonnegligible off-chain component to the spin dynamics, which can be further investigated by the EPR of $[CH]_x$ of different molecular weights (MW).

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