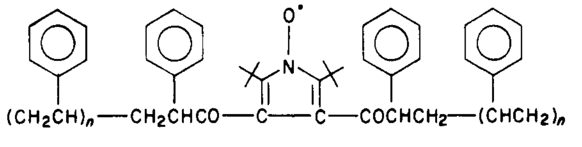

The long correlation time measured in samples of copolymer II corresponds to the presence of main-chain double bond which slows down the local segmental motion of the polystyrene chain.

The effect of the double bond on the segmental motion can be treated on the analogy of crankshaft transitions of the polystyrene chain. The number of monomer units involved in the relaxation process can be obtained according to the treatment described in detail by Mashimo[13] and Friedrich et al.[1] On the basis of Kramers'[14] and Helfand's[15] theory (in the limit of high viscous damping and for the crankshaft motion) the correlation time is related to the solvent viscosity η and the temperature T

$$\tau_c \sim \frac{2\pi}{\gamma}\sum_i r_i^2 \xi_i \exp(E^*/RT)$$

where E^* is the height of the internal potential barrier for the rotational motion of monomer units. The potential barrier has a form $U = {}^1/_2E^*(1 - \cos 3\theta)$ with the curvature $\gamma = \mathrm{d}^2U/\mathrm{d}\theta^2$ in its minimum and maximum, r_i is the distance of the ith monomer unit from the shaft, and ξ_i is the frictional coefficient. If the monomer unit is treated as a sphere of radius a, then $\xi_i = 6\pi a\eta$ according to the Stokes law. Using a value of 3 Å for a[13] and $E^* = E - E_\eta = 7.69$ kJ/mol, where $E_\eta = 8.69$ kJ/mol is the activation energy for the viscosity of toluene,[1] we obtain

$$24\ \text{Å}^2 < \sum_i r_i^2 < 73\ \text{Å}^2$$

The mean of r_i cannot be affected significantly by the double bond; therefore it is taken to be 4 Å according to the literature.[11,13,16] Consequently, the motion of the label in structure II is analogous to the crankshaft motion of the chain in which 2–4 monomer units are involved, in contrast to the case of unlabeled polystyrene as well as spin-labeled polystyrene without a double bond, where only one monomer unit is involved in the ^{13}C NMR and ESR relaxation processes.[1]

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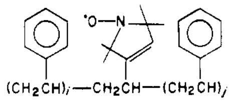

In this case a short correlation time is expected which should be close to the value for spin-labeled polystyrene measured by Bullock et al.[2]
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Sequence Distribution of Carboxyl Groups in Hydrolyzed Polyacrylamide

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ABSTRACT: A carbon-13 NMR study of hydrolyzed polyacrylamides has demonstrated that mild alkaline hydrolysis provides a well-spaced distribution of carboxyl groups along the polymer chain. This distribution is somewhat a function of ionic strength during hydrolysis, supporting an electrostatic component in resolution of rate constants. Acid hydrolysis, on the other hand, tends to develop blocks of carboxyl groups. A combination of the two modes suggests the possibility of developing controlled blocks of carboxyl groups along the chain.

Introduction

Fundamental correlations of polymer structural effects on interaction of flocculants with clays require knowledge of the microstructure of polymers. Unfortunately, many publications make tacit assumptions in this area and then look for effects. Although it is generally believed that alkaline hydrolysis of polyacrylamide provides a relatively uniform distribution of carboxyl groups along the polymer chain, evidence has been indirect.[1–5] The present investigation provides a relatively direct, quantitative measure of the sequence distribution generated under mild, homogeneous hydrolysis conditions, using carbon-13 NMR spectroscopy. These polymers, and others differing only in molecular weight, are being used in studies on flocculation of clays. Carboxyl heterogeneity which can develop between chains is discussed elsewhere.[6]

Experimental Section

All the hydrolyzed polymer samples used in this study were obtained from the same sample of homopolymer, designated 8103-88. It had been prepared by free-radical solution polymerization in water at 40 °C, using acrylamide recrystallized from chloroform, an ammonium persulfate–sodium metabisulfite catalyst system, and 2-propanol as a chain-transfer agent. The viscosity-average molecular weight (obtained via capillary viscometry and a Mark–Houwink equation[7]) was 6.6 × 10^5 daltons, and the number-average molecular weight was (2.5–3.0) × 10^5 daltons (obtained via osmometry). A 5% aqueous solution of the homopolymer was flushed with nitrogen; 2-propanol was added to the solution to the extent of about 2%, followed by the stoichiometric amount of 10% sodium hydroxide solution for the degree of hydrolysis desired. This mixture was kept at 43–46 °C for 18–24 h, then cooled, and freeze-dried. Samples thus prepared formed a coherent set in terms of (a) the same molecular weight, (b) a molecular weight suitable for use in carbon-13 studies, and (c) a stepwise range of anionicities (less than 0.5 to about 33 mol%).

Hydrolyses to about 35 and 66 mol% were the same as above except the solvent system was 0.75 M NaCl (samples 8303-04 and -05). Hydrolysis to 55 mol % carboxyl utilized a 9 wt % polymer solution and 30% NaOH solution (sample 8302-01). Two hydrolyses were carried out by using a concentrated aqueous ammonia solution, as a check on the effect of choice of base. The poly(acrylic acid) sample was a commercial product (Aldrich Catalog No. 19,205-8, with a reported molecular weight of about 90 000 daltons). Aqueous solutions containing about 10 wt % polymer were neutralized with excess base (NaOH, LiOH, KOH, or NH_3).

Acid hydrolyses were carried out by mixing a 5% aqueous solution of polymer with the stoichiometric amount of 6 N HCl and placing in an oven at 95 °C for 16–18 h. The precipitated gel (insoluble because of the low pH and cyclic imide formation[8]) was isolated and mixed with enough water to develop an 8–10% solution when solubilized, and sufficient 10% NaOH to hydrolize the imide was added. This mixture was placed in an oven at 95 °C for varying times up to 24 h. The resulting solutions were cooled, and the pH was adjusted to 8.5 with sodium hydroxide before measurements were made. Glutarimide was purchased from Aldrich, Catalog No. 17,809-8.

Carboxyl levels were determined by analysis of infrared absorption bands due to the amide carbonyl and to the carboxylate anion in thin films. Calibration was established via reference samples. Results generally agreed with that calculated via stoichiometry within about 3% on an absolute basis (such as 33% vs. 30%). An independent check also existed in the NMR data, as shown in the text.

Carbon-13 spectra of samples designated 8103-88, and 8104-62–8104-64 were obtained at 100.62 MHz with a Bruker WH400 spectrometer, at 70 °C. Spectra of the remaining samples were obtained at 50.309 MHz with a Varian XL200 spectrometer. For these the sample temperatures generally were in the range 30–70 °C because of variations in the heating effects of the decoupling irradiation. Pulse widths were in the range 45–60°, acquisition times were either 0.8 or 1.0 s, and no pulse delay was used between pulses. Approximately 60 000 transients (an overnight run) were accumulated for each spectrum. Because of the low signal/noise ratio, gated-decoupling procedures, which would involve a long pulse delay, were not used. The method outlined in the discussion section was selected to ensure quantitative results. Solution concentrations generally were about 8–10 wt % polymer, pH adjusted to 8.5, with sufficient D_2O added as a lock signal. Chemical shifts vs. Me_4Si were established by referencing to dioxane at 67.40 ppm. Line intensities were obtained by integrating the intensity vs. chemical shift curve. Deconvolution of overlapping lines was done visually and thus introduced a degree of subjectivity into the value obtained. Except for badly overlapped lines and for very weak absorption, it is believed the relative intensities are within 5–10% of the true values. Addition of NaCl to the solutions did not affect line positions or intensities significantly. The spectrum of glutarimide was obtained in a Me_2SO solution, as well as were a few other samples to obtain a rough check on the line shifts when changing solvents. (Glutarimide is not sufficiently soluble in water.)

Longitudinal relaxation times were measured by the standard inversion recovery method, utilizing an equilibration delay time of 8 s after each 180°– τ –90° sequence. For our experimental conditions of sample handling and preparation, at a concentration of about 18 wt % polymer, values obtained were 1.9–2.0 s for the amide carbonyl carbon, and 2.7–2.8 s for the carboxylate anion carbon. There were indications that both relaxation times might be slightly longer at 5 wt % polymer, but since there was more scatter in data at the lower concentration and since the apparent difference did not materially affect later uses of T_1, this aspect was not explored in detail. Values around 0.22–0.23 s were obtained for the methine carbon atoms, whether adjacent to an amide group or to a carboxylate anion. Nuclear Overhauser enhancement (NOE) factors were found to be about 2.2 for the two types of carbonyl carbon atoms, and about 2.6 for the methine carbon atoms.

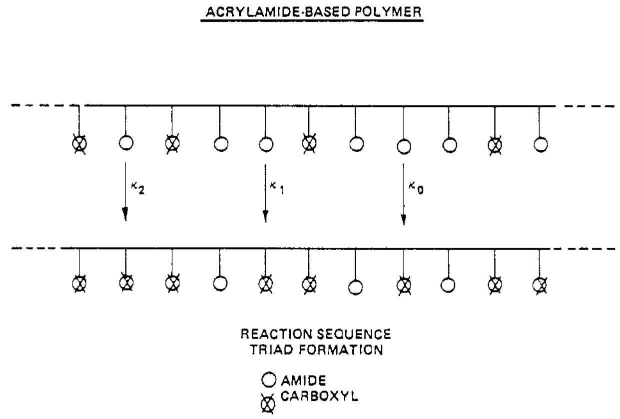

Figure 1. Kinetic scheme for hydrolysis of polymer (subscripts on rate constants for amide group hydrolysis, k, indicate number of nearest-neighbor carboxyl groups).

Results and Discussion

Alkaline Hydrolysis. Kinetics of alkaline hydrolysis of polyacrylamide suggest neighboring-group catalysis,[1–5] superimposed on a general electrostatic effect. A schematic description of primary rate constants for attack of an OH^- at a polymer amide grouping, for zero, one, or two nearest-neighbor carboxylate groups, is given in Figure 1. Indirect evidence would suggest $k_0 > k_1, k_2$. The main tool for determination of sequence distributions in a number of polymers, however, has been carbon-13 NMR spectroscopy.[9–13] The present study provides direct information regarding sequences in products obtained by relatively mild homogeneous hydrolysis conditions.

In order to examine the spacing of carboxyl entities along the chain, let us consider sequences of three monomer units, the triad structure. If we designate an acrylamide segment by A, and the sodium salt of a hydrolyzed acrylamide by B, the six unique triads are AAA, AAB = BAA, BAB, BBB, ABB = BBA, andd ABA. Current sample preparation techniques and instrumentation allow resolution of the triad structure in the carbonyl carbon-13 NMR spectrum of the materials in the present study, that is, the effect due to nearest neighbors, but shifts due to next nearest neighbors are questionable. Our peak assignments for the carbonyl carbon of the central monomer for the various triads are given in Table I, along with a designation of the polymers used. Traces of the experimental intensity vs. chemical shift curves are given in Figure 2 for typical samples (8103-88, 8104-62–8104-64).

Triad structure is not resolved in our carbon-13 NMR spectra for the methine carbon atoms, although the peak for the methine carbon of the acrylamide segment is well separated from the sodium acrylate segment (43.2 vs. 45.7 ppm). In view of the same relaxation times and NOE factors, however, the relative intensities of these two types of methine groups provide an ideal internal measure of the total carboxyl level in the polymer sample. Values thus obtained are consistent with data obtained by other techniques.

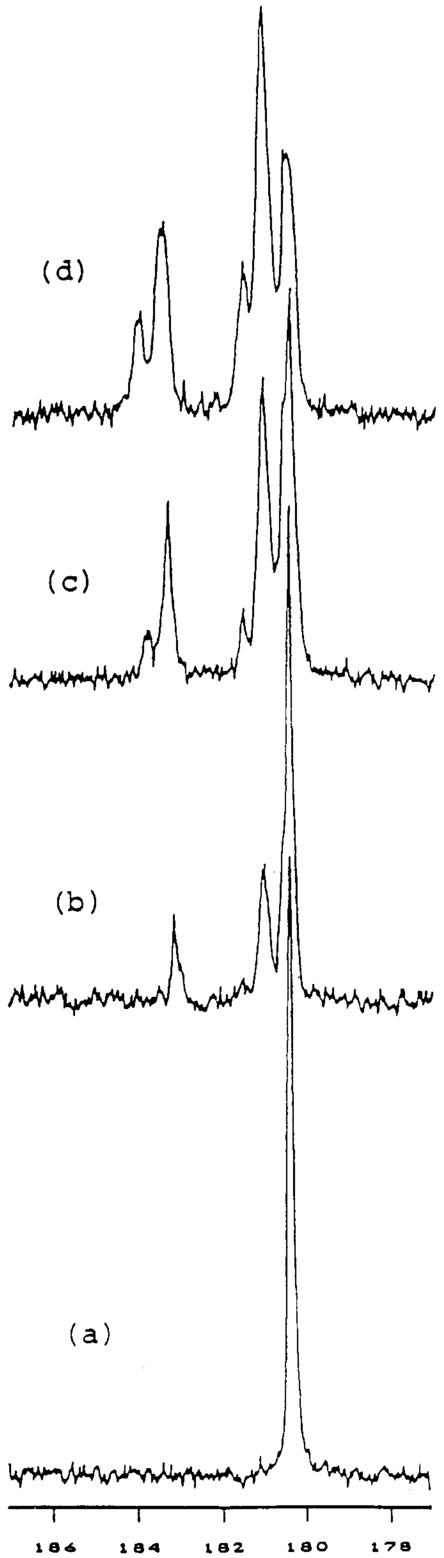

Figure 2. Carbon-13 NMR signal intensity vs. chemical shift (alkaline hydrolysis: (a) homopolymer, (b) 10% hydrolyzed, (c) 22% hydrolyzed, (d) 33% hydrolyzed).

Let us designate the mole fraction of A units having only A units as nearest neighbors by $F(\mathrm{AAA})$, the mole fraction of A units having one A unit and one B unit as neighbors by $F(\mathrm{AAB})$ or $F(\mathrm{BAA})$, and so forth. These triad mole fractions neglect all aspects of next nearest neighbors. In order to utilize our measured relative intensities of the NMR lines for the carbonyl atoms to provide values for these mole fractions, however, data on relaxation times and NOE factors must be considered in relationship to our standard experimental procedures. Insofar as the $F(\mathrm{AAA})$, $F(\mathrm{AAB})$, and $F(\mathrm{BAB})$ ratios are concerned, or the $F(\mathrm{BBB})$, $F(\mathrm{BBA})$, and $F(\mathrm{ABA})$ ratios, the raw intensity data can provide correct information. On the other hand, when making comparisons between these groups, differences in relaxation times for the central carbon atoms require that a correction factor be applied to the raw data. There are at least two ways to arrive at the correction factor. One is basically empirical. Designate the experimental integrated intensity for the ith line by E_i. Let the first three lines represent the A-centered triads, and the next three the B-centered triads. Normalize the true relative intensities, I_i, to those for the amide carbonyl carbon, that is, $I_1 = E_1$, $I_2 = E_2$, and $I_3 = E_3$. Then $I_4 = CE_4$, $I_5 = CE_5$, and $I_6 = CE_6$, where C is the correction factor. Using the mole fraction of carboxyl groups in the polymer obtained from the methine lines or the infrared data, designated by MA, one has the relationship

$$\mathrm{MA} = \frac{C\sum_{i=4}^{6} E_i}{\sum_{i=1}^{3} E_i + C\sum_{i=4}^{6} E_i}$$

Consequently C is given by the expression

$$C = \frac{\mathrm{MA}\sum_{i=1}^{3} E_i}{(1 - \mathrm{MA})\sum_{i=4}^{6} E_i}$$

Values of C obtained this way generally are in the range 1.20–1.36. This approach is analogous to that used in a study on solution chlorinated polyethylene.[13]

Another approach is to consider details of the NMR measurement procedure. Since the NOE factor is essentially the same for both types of carbonyl carbon atoms, the equation[14]

$$\frac{M(\tau)}{M_0} = \frac{(1 - \exp(-\tau/T_1))\sin\theta}{(1 - \cos\theta\exp(-\tau/T_1))}$$

can be used. It is appropriate for the steady-state magnetization in the case of an infinite sequence of pulses, where τ is the separation between pulses and θ is the tip angle. When we substitute our values for τ and T_1, and take $\theta = 60°$ or $45°$, the intensity correction for B-centered triads falls in the range 1.22–1.33. The agreement between the two approaches is gratifying, as is the agreement with carboxyl level determined by other means. A value of about 1.26 was used to convert raw relative intensities to mole fractions for Tables II and IV. One notes in Table II that there is no significant difference for the samples hydrolyzed with ammonia relative to those hydrolyzed with NaOH. For comparison purposes, similar data are given for a copolymer of acrylamide with 30 mol % sodium acrylate (polymerized at pH about 5).

If hydrolysis of the amide groups had occurred completely at random along the polymer chain, that is, was unaffected by proximity to a carboxylate ion, the distribution would be as indicated in Table III for $K = k_1/k_0 = 1$, $L = k_2/k_0 = 1$. Data in Table II show the carboxyl groups are well distributed along the chain, certainly more widely spaced than a random distribution and slightly more than for the copolymer examined. This result is in essential agreement with data reported on glass transition temperatures for hydrolyzed polymers and for a copolymer.[15] Since these samples were hydrolyzed under strictly homogeneous conditions, the carboxyl level should

Table I
Peak Assignments

sample	acid	chem shift,[a] ppm AAA	AAB	BAB	ABA	BBA	BBB
Na							
8103-88	<0.5	180.34					
8104-62	10	180.35	180.97		183.13		
8104-63	22	180.37	181.01	181.55	183.31	183.76	
8104-64	33	180.42	181.06	181.56	183.40	184.14	
8302-01	55		181.20	181.60	184.04	184.54	184.98
8303-05	35	180.39	180.92	181.47	183.57	184.14	184.90
8303-04	66+			181.60	183.82	184.41	184.92
NH_3							
8303-02	10	180.37	180.96		183.6		
8303-03	18	180.42	180.96	181.46	183.64	184.32	
NaPAA							
8303-01	100						185.38

[a] Dioxane = 67.4 ppm.

Table II
Mole Fractions via NMR[a]

sample	acid	mole fraction AAA	AAB	BAB	ABA	BBA	BBB
Na							
8103-88	<0.5	1.0					
8104-62	10	0.68	0.20		0.12		
8104-63	22	0.44	0.30	0.03	0.19	0.04	
8104-64	33	0.21	0.38	0.09	0.22	0.10	
8302-01	55		0.10	0.32	0.22	0.36	<0.01
8303-05	35	0.15	0.44	0.07	0.24	0.09	0.01
8303-04	66+			0.35	0.14	0.43	0.08
NH_3							
8303-02	10	0.68	0.19		0.12		
8303-03	18	0.45	0.34	<0.01	0.18	0.02	
NaPAA							
8303-01	100						1.0
CoPOL	30	0.36	0.32	0.02	0.12	0.19	

[a] Alkaline hydrolysis.

Table III
Mole Fractions Calculated[a]

acid[b]	K, L	mole fraction F(AAA)	F(AAB)	F(BAB)	F(ABA)	F(BBA)	F(BBB)
10	1.0, 1.0	0.729	0.162	0.009	0.081	0.018	0.001
	0.5, 0.25	0.716	0.169	0.010	0.089	0.010	
	0.3, 0.02	0.713	0.173	0.010	0.093	0.007	
	0.2, 0.04	0.714	0.175	0.010	0.095	0.005	
	0.2, 0.002	0.713	0.175	0.010	0.095	0.004	
	0.1, 0.01	0.713	0.177	0.011	0.098	0.002	
20	1.0, 1.0	0.512	0.256	0.032	0.128	0.064	0.008
	0.5, 0.25	0.485	0.277	0.039	0.156	0.041	0.002
	0.3, 0.02	0.470	0.287	0.042	0.172	0.028	
	0.2, 0.04	0.464	0.293	0.043	0.180	0.020	
	0.2, 0.02	0.463	0.293	0.043	0.180	0.020	
	0.1, 0.01	0.456	0.299	0.045	0.189	0.011	
30	1.0, 1.0	0.343	0.294	0.063	0.147	0.126	0.027
	0.5, 0.25	0.296	0.321	0.083	0.197	0.093	0.010
	0.3, 0.02	0.268	0.336	0.096	0.231	0.066	0.003
	0.2, 0.04	0.255	0.344	0.100	0.247	0.051	0.002
	0.2, 0.002	0.254	0.344	0.101	0.248	0.050	0.002
	0.1, 0.01	0.238	0.354	0.108	0.271	0.029	
50	1.0, 1.0	0.125	0.250	0.125	0.125	0.250	0.125
	0.5, 0.25	0.068	0.241	0.192	0.195	0.235	0.069
	0.3, 0.02	0.029	0.209	0.263	0.261	0.212	0.027
	0.2, 0.04	0.019	0.210	0.270	0.280	0.191	0.029
	0.2, 0.02	0.017	0.202	0.281	0.287	0.191	0.022
	0.1, 0.01	0.004	0.182	0.313	0.324	0.161	0.015

[a] $K = k_1/k_0$; $L = k_2/k_0$. [b] Percent hydrolysis, as in previous tables.

be uniform between chains.[6]

Average values for mole fractions of triads, calculated for other values of the K, L parameters, are given in Table III also. Values for the A-centered triads were calculated by using the kinetic formulation for neighboring-group effects developed by Boucher.[16] Values for the B-centered triads were calculated by using the B-approximation of Plate and co-workers[17] to formulate equations for dF-

Table IV
Mole Fractions via NMR[a]

	mole fraction						
sample	AAA	AAB	BAB	ABA	BBA	BBB	imide
82-71	0.45	0.19		0.07	0.08	0.05	0.16
82-72	0.45	0.27		0.13	0.09	0.03	0.03
82-81	0.35	0.35		0.16	0.10	0.04	0.00

[a] Acid hydrolysis + base; see text.

(ABA)/dF(B), dF(BBA)/dF(B), and dF(BBB)/dF(B), which then were solved numerically. (Values in the third decimal place are uncertain.) No serious attempt was made to minimize simultaneous differences between calculated and observed triad distributions via variations in the parameters K and L, since K and L are sensitive to ionic strength of the medium.

Comparison of Table III with Table II shows that neighboring groups exert a considerable effect on the distribution. The resolution of k into k_0, k_1, and k_2 presumably results from a number of factors, but one certainly is an electrostatic effect of the carboxylate anion. It consists of both a Coulombic repulsion (with respect to an approaching hydroxyl ion) and a conformational factor (for the polymer chain). There is a literature report on the effect of sodium hydroxide level on the rate of hydrolysis of polyacrylamide which suggests the possibility of next-nearest neighbor interactions[3], although validity of the data has been questioned in another publication.[5] A slight modification of the kinetic scheme of Figure 1 would be required, where each of k_0, k_1, and k_2 would be resolved into three components, for zero, one, or two carboxylate anions in the next-nearest-neighbor positions.

Our normal hydrolysis procedure results in near minimal ionic strength of the reaction medium (comparable to the lower ionic strength of ref 3), and so electrostatic effects should be at their maximum. Sample 8302-01 was hydrolyzed in an intermediate ionic strength medium, and samples 8303-5 and -04 in a higher ionic strength medium. The most obvious result is a distinct increase in BBB triads at high ionic strength, which supports the existence of an electrostatic effect. (In Table II a designation <0.01 means that a line is observed, but the intensity is so low that a measurement is subject to large errors. On the other hand, the value 0.01 means a significant presence, although the absolute value should be treated with caution. Indeed, magnitudes less than 0.05 are not very accurate.) There is no accompanying increase in BBA triads, however, and the implications of this observation are under study. This dependence of relative rates on ionic strength, however, negates any precise determination of K and L from our data, since electrolyte levels were variable. Nor do we have sufficient data under controlled electrolyte levels to establish whether next nearest neighbors exert a significant effect on relative rate constants.

Acid Hydrolysis. Several preliminary hydrolyses were carried out in a dilute polymer solution with hydrochloric acid, which also develops intramolecular imide groups.[8] This was followed by treatment with NaOH to convert some imide groups to carboxylate ions and confer solubility. The NMR chemical shift for the imide carbonyl carbon in these samples occurred at 178.49 ppm, and the spectrum for sample 82-71 is reproduced in Figure 3. Since hydrolysis of the imide groups involved conditions favorable to alkaline hydrolysis of amide groups also, the sequence distribution is the result of a number of reactions. Observed triad mole fractions are given in Table IV for a sample in which about 20–30 mol % of the amide groups had been reacted, and with varying degrees of hydrolysis of imide groups. (Here it is assumed the intensity behavior of the imide carbonyls is the same as for the amide carbonyl.) One notes a significant fraction of BBB triads, along with an absence of BAB triads, which is particularly noticeable for sample 82-71 (before the more complete alkaline hydrolyses of the imide). Subsequent samples tend to add triads much the same as for normal alkaline hydrolysis, with little change in BBB and ABB triads (within experimental error). Thus, catalysis due to neighboring carboxyl groups occurred during acid hydrolysis, in support of kinetic studies.[18] This aspect is being investigated in more detail, with particular attention to the possibility of preparation of anionic polymers having controlled blocks of carboxyl groups.

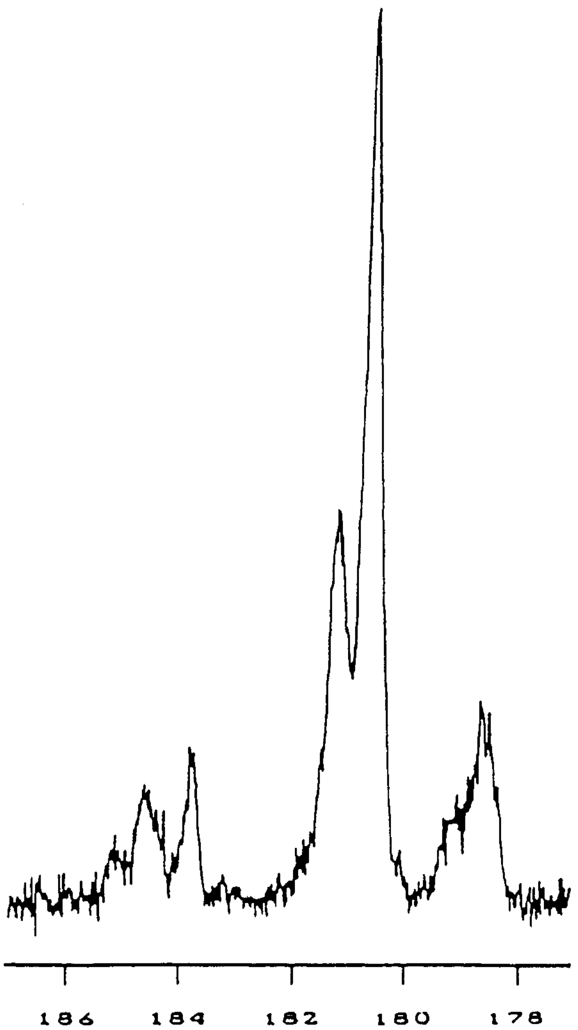

Figure 3. Carbon-13 NMR signal intensity vs. chemical shift (acid hydrolysis followed by alkaline hydrolysis; see text).

Although imide formation is well-known during strong acid hydrolysis of polyacrylamide, its existence during alkaline hydrolysis also has been reported in the literature.[19] Within the confines of our procedures, however, we did not detect any in the samples examined in this study.

Conclusions

Mild alkaline hydrolysis, such as used in our normal procedures, produces anionic polymer with the anionic sites well spaced along the polymer chain. Thus, these products are suitable for detailed studies on polymer interactions with clays as an example of one type of microstructure. High ionic strength during alkaline hydrolysis, however, significantly moderates the electrostatic effect of anionic sites on neighboring hydrolysis sites. Strong acid hydrolysis, on the other hand, tends to develop blocks of anionic sites. A combination of these factors suggests that conditions may exist for controlled generation of blocks of anionic sites along the polymer chain. It appears necessary to minimize imide formation during this process.

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Determination of Branches in Terpolymers of Ethylene, 1-Butene, and Long α-Olefin by Pyrolysis–Hydrogenation–Gas Chromatography

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ABSTRACT: Pyrolysis–hydrogenation–gas chromatography (PHGC) was applied to determine the branches in ethylene–1-butene–α-olefin terpolymers, where α-olefin was 1-decene, 1-dodecene, or 1-hexadecene. The polymers were prepared by using Ziegler–Natta catalysts in *n*-heptane suspension. Each branch type was identified from the characteristic methylalkane peak caused by β-scission of the branched carbon. Quantitative determinations were done by using ethylene–α-olefin copolymers as reference. Octyl, decyl, and tetradecyl branches were identified from the pyrograms. Branch contents determined by the PHGC technique were compared with those obtained by IR and ^{13}C NMR spectroscopy. Few scissions were observed in the branches of the copolymers.

Introduction

The length and distribution of branches have a substantial effect on the properties of polyethylene. Melt properties and solution viscosity are predominantly affected by long-chain branches, whereas crystallinity, density, crystalline melting temperature, stiffness, hardness, gas permeability, and chemical resistivity are related to short-chain branches.[1-3] In order to regulate polyethylene properties, it is important to produce branches under controlled circumstances, analyzing their concentrations and distributions. Coordination polymerization permits the production of desired branches using α-olefins as comonomers. α-Olefins containing 4–8 carbon atoms are commonly used commercially, though it is possible to use longer α-olefins. IR[4-6] spectroscopy and ^{13}C NMR[7-19] spectroscopy are generally the applied methods for characterization of chain branching in polyethylene. These methods are limited, however. For example, total branch content can reliably be measured by IR spectroscopy, but it cannot be used for characterization of different branch types. Ethylene–α-olefin copolymers prepared with known α-olefins have been widely studied by ^{13}C NMR spectroscopy[7,8,11,13,14] and the results applied to the determination of LDPE branches.[4,7,8,10,12-16] Branches from methyl to amyl can be measured individually by ^{13}C NMR spectroscopy, though branches of six or more carbon atoms cannot be differentiated. The quantitative analysis can be done from peak intensities of typical carbon atoms for different branches.[17-19]

Recently, pyrolysis–hydrogenation–gas chromatography (PHGC) has become a useful complement to IR and ^{13}C NMR spectroscopy for the characterization of poly-

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