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(15) Poly(ferrocenylenes) of previous investigations[2,5,16] were found to contain [0.0]ferrocenophane (bisfulvalenediiron) in variable proportions resulting from Cu- or Co-assisted internal cyclization of dinuclear intermediates.

(16) L. Bednarik, R. O. Gohdes, and E. W. Neuse, *Transition Met. Chem.*, **2**, 212 (1977).

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(18) E. C. Ashby and J. J. Lin, *J. Org. Chem.*, **42**, 2805 (1977). Although organocuprates with Li/Cu > 2 are unknown, such cuprates may well exist in mixtures possessing high relative organolithium contents.

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(25) D. Steele and D. H. Whiffen, *Trans. Faraday Soc.*, **55**, 369 (1959).

(26) 1,4-Diferrocenylcyclopenta-1,3-diene gives peaks at 3.40 and 6.38 ppm, and 1-ferrocenylcyclopentene resonates at 1.8–2.6 and 5.8 ppm (in $CDCl_3$).

(27) In accord with the absence of substitution reactions involving the solvents, we were unable to detect alkylated or alkoxylated ferrocenes in the mass spectra of oligomeric material, e.g., fractions III and IV.

(28) 1,2-Terferrocenyl gives distinctly reduced extinction coefficients and maxima blue shifted by some 5 nm relative to the 1,1′ isomer.[22b]

(29) S. I. Goldberg and J. G. Breland, *J. Org. Chem.*, **36**, 1499 (1971); P. V. Roling and M. D. Rausch, *J. Organomet. Chem.*, **141**, 195 (1977).

(30) The 1,3-trimer, 1,3-diferrocenylferrocene,[22c] likewise resonates near 4.4 ppm, and so probably do higher homologues containing a 1,3-disubstituted ferrocene group as could have arisen from a 1,3,1′-trilithioferrocene. Although some 1–2% of trilithiated ferrocene has been found to be present in the lithiation mixture under our experimental conditions, the absence of resonances near 4.4 ppm in the crude trimer (and also in the crude tetramer) fractions suggests the contents of such trilithiated intermediate to be too small to bring about any detectable degree of incorporation of 1,3-disubstituted groups (or 1,3,1′-trisubstituted branch point units) into the polymer chain.

(31) The tetra-, penta-, and hexameric homologues of 3 are too poorly soluble[20] to permit their isolation by the conventional fractionating precipitation techniques. For this reason they were removed from the crude polycondensation product mixture by extraction and crystallization operations (fractions III) as detailed in the Experimental Section and hence were essentially absent in the material subfractionated.

Sulfonation of a Polypentenamer and Preparation of Its Hydrogenated Derivatives

D. Rahrig,[†] W. J. MacKnight,*[†] and R. W. Lenz[‡]

Polymer Science and Engineering Department and Chemical Engineering Department, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003. *Received November 17, 1978*

ABSTRACT: Polypentenamer has been sulfonated using a 1:1 complex of sulfur trioxide and triethyl phosphate in chloroform. A range of polymers containing from 1.9 to 19.1 mol % sulfonate groups was prepared by this reagent and isolated in the form of sodium salts. These materials are initially free from covalent cross-links but cross-linking occurs with aging unless the polymers are stabilized with a free-radical scavenger such as hydroquinone. The unsaturated bonds in these materials can be removed by hydrogenation with *p*-toluenesulfonyl hydrazide. The hydrogenated derivatives are crystalline and no longer require a stabilizer to inhibit cross-linking. Both the unsaturated and hydrogenated polymers are hydrophilic.

The chemical modification of a polypentenamer by hydrogenation,[1] hydroformylation,[2] the addition of thioglycolate side groups,[3] and phosphorylation[4] has been previously reported from this laboratory. The objective of these studies has been the preparation of polymer derivatives containing side groups of differing chemical nature and concentration but with identical chain backbones. It has thus been necessary to carry out the reactions under conditions which preclude backbone modification by scission or cross-linking. The present work has been concerned with sulfonating polypentenamer using a 1:1 complex of sulfur trioxide and triethyl phosphate and isolating the resulting product in the form of the sodium salt. The residual double bonds in the sulfonated polypentenamer can be subsequently hydrogenated, as was previously done with the other derivatives, to yield a crystalline polyethylene derivative.

While the preparation of sulfonated polymers is an area where much effort has been directed,[5-9] the preparation of a stable, highly unsaturated, highly sulfonated polymer free from covalent cross-links has not been previously reported. Even for polymers with fully saturated backbones, sulfonation reactions generally lead to the formation of some covalent cross-links,[10,11] quite often in the form of sulfone linkages.[5,10] The reagents used in sulfonation reactions can, in most cases, be regarded as sulfur trioxide based compounds or complexes, with the reactivity of the SO_3 being regulated by the nature of the reagent.[12]

In recent years, complexes of sulfur trioxide with trialkyl phosphate having SO_3 to trialkyl phosphate ratios ranging from 2:1 to 4:1 have permitted the preparation of sulfo-

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[†] Polymer Science and Engineering Department.

[‡] Chemical Engineering Department.

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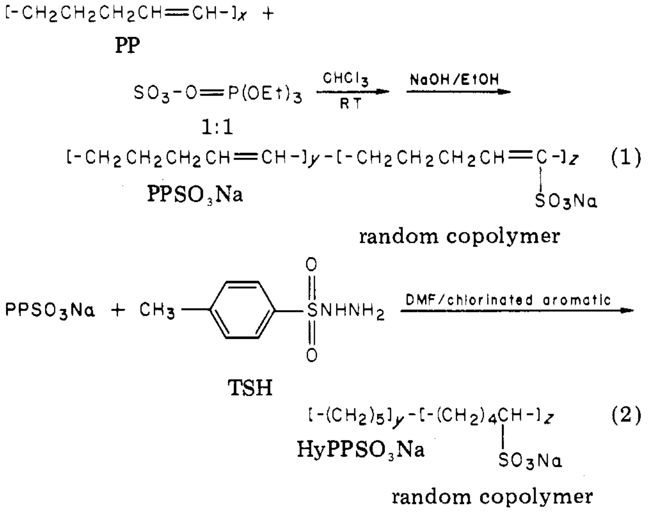
nated polymers free from covalent cross-links.[8,13,14] These cases have generally involved the sulfonation of aromatic rings, although Canter was successful in sulfonating butyl rubber polymers and in sulfonating more highly unsaturated elastomers to low degrees of sulfonation.[8] Turbak has demonstrated[15] that 1:1 complexes of SO_3 with trialkyl phosphates are reactive enough to successfully sulfonate long chain α-olefins. More importantly it was observed[15,16] that under the proper reaction conditions, these complexes will yield exclusively alkene sulfonates, while all other SO_3 complexes are known to give a mixture of products.[12] These factors suggest that the 1:1 SO_3–trialkyl phosphate complex might be a suitable reagent for sulfonating polypentenamer, a proposal borne out by the results of this study.

The sulfonated polypentenamers and their hydrogenated derivatives can be prepared by the following synthetic route:



PP

1:1

PPSO₃Na (1)

TSH

HyPPSO₃Na (2)

The degree of sulfonation for the polymers in this study ranged from 1.9 to 19.1 mol %, based on the polypentenamer repeat unit. Over this range of substitution significant changes in properties are observed. The unsaturated polymers vary from very rubbery materials to very tough, leathery materials as the degree of sulfonation is increased. The hydrogenated polymers, on the other hand, become more rubbery with increasing sulfonation due to the corresponding decrease in crystallinity. In both cases, water greatly alters the properties of the highly sulfonated polymers.

Experimental Section

Materials. Polypentenamer (PP). This polymer was kindly provided by the Goodyear Tire and Rubber Co. It contains 82% trans and 17% cis double bonds with less than 1% vinyl side groups. The molecular weight averages are $\bar{M}_n = 172\,000$ and $\bar{M}_w = 470\,000$ for this starting material.

Reagents. Liquid sulfur trioxide was purchased from Research Inorganic Chemical Corp. It was distilled using a steam-heated condenser to prevent the formation of α-form crystals of SO_3. Triethyl phosphate (TEP) was purchased from Aldrich Chemical Co. and vacuum distilled before use. The p-toluenesulfonyl hydrazide (TSH) was purchased from Aldrich Chemical Co. and was recrystallized from ethanol before use. Sodium hydroxide and hydroquinone were used as received.

Solvents. Chloroform was distilled over phosphorus pentoxide and stored over molecular sieves until use. Dimethyl formamide was vacuum distilled over calcium hydroxide and also stored over molecular sieves until use. All other solvents were purified by standard procedures.

Preparation of the SO_3/TEP Complex. Under a dry N_2 atmosphere, a three-necked reaction flask was charged with 6.6 mL (0.038 mol) of triethyl phosphate and 20 mL of chloroform. The reaction flask was fitted with a dropping funnel which was charged with 1.6 mL (0.038 mol) of freshly distilled sulfur trioxide. The reaction vessel was cooled to 0 °C with an ice–water bath and the SO_3 was added dropwise to the triethyl phosphate/chloroform solution. After all of the SO_3 was added, the reaction mixture was allowed to come to room temperature.

Sulfonation of Polypentenamer. A three-necked reaction flask was fitted with a dropping funnel, an N_2 inlet, and a drying tube pressure outlet. The flask was charged with a 1–2% (w/v) solution of purified polypentenamer in chloroform. The dropping funnel was charged with an appropriate amount of the SO_3/TEP complex solution and diluted with additional chloroform. Under N_2 flow and with vigorous stirring the SO_3/TEP complex solution was added dropwise to the polypentenamer solution. The reaction was allowed to progress for 2 h after all of the complex solution was added. At that time the reaction mixture was poured into a 0.25 M solution of NaOH in ethanol. The precipitated polymer was washed several times with distilled water and ethanol, stored overnight in another 0.25 M solution of NaOH in ethanol, then washed extensively with distilled water and ethanol. Finally, the product was allowed to stand overnight in a 0.1 M solution of hydroquinone in ethanol. The sulfonated polypentenamer was dried in a vacuum oven at room temperature for several days, then stored in a desiccator under vacuum until use.

Hydrogenation of Sulfonated Polypentenamer. The sulfonated polypentenamer was put into a mixed solvent system of dimethyl formamide (DMF) and either chlorobenzene or 1,2,4-trichlorobenzene (the ratio of DMF to the chlorinated benzene varying as the degree of sulfonation varied) and dissolved with moderate heating under N_2 flow. Once dissolved the polymer solution was cooled to 80 °C and enough purified p-toluenesulfonyl hydrazide was added to give a 2:1 ratio of TSH to PP repeat units. The reaction mixture was then heated to 130–135 °C and maintained at this temperature for 2 h. At that time the reaction mixture was poured into acetone and the hydrogenated, sulfonated polypentenamer precipitated out of solution. The product was filtered, washed several times with ethanol and water, then dried overnight in a vacuum oven at room temperature. The dry product was then put back into a DMF/trichlorobenzene solution and the hydrogenation step repeated using the same quantity of TSH employed in the first reaction. The product was again precipitated into acetone, washed extensively with distilled water, ethanol, and acetone, and dried several days in a vacuum oven at room temperature. The dry product was then stored in a desiccator under vacuum until use.

Characterization. The samples were characterized by elemental analysis, infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), and thermal gravimetric analysis (TGA) as follows:

Elemental Analysis. Elemental analysis of the sample was performed by the Analytical Services and Microanalytical Laboratory, University of Massachusetts. The degree of sulfonation was based on the sulfur to carbon ratio of these analyses, while the percent neutralization was based on the sodium to sulfur ratios determined.

IR Measurements. Solvent cast films of the polymers were prepared on NaCl plates. IR spectra were recorded on a Perkin-Elmer Model 283 grating infrared spectrophotometer. The determination of sulfonate group content was based on the ratio of the absorption band at 1045 cm^{-1} (O=S=O symmetric stretch) and either the 1420-cm^{-1} band (backbone methylene stretch) or the 965-cm^{-1} band (trans C=C) using standard calibration procedures.

NMR. NMR measurements on the samples were carried out on a Perkin-Elmer Model R32 NMR spectrometer in dimethyl-d_6 sulfoxide using HMDS as an external standard.

TGA. TGA measurements were carried out on a Dupont 950 thermogravimetric analyzer in conjunction with a Dupont 900 thermal analyzer. Measurements were performed in a nitrogen atmosphere at a scanning speed of 20 °C/min in all cases.

Differential Scanning Calorimetry (DSC). DSC measurements were carried out on a Perkin-Elmer Model DSC II. The scanning speed was 20 °C/min in all cases and indium was used as a calibration standard. The temperature range was from −120 to 150 °C for the unhydrogenated samples, and from −40 to 180 °C for the hydrogenated samples. The temperature of maximum

Table I
Reaction Conditions^a for Sulfonating Polypentenamers

sample	PP, mol	complex, mol^b	$CHCl_3$, mL	time, h	%^{e} of sulfonation	%^{f} of conversion	%^{g} of neutralization
X-8A	0.104	0.0053	700^c	16.0	1.9	37	89
X-8B	0.104	0.0104	700^c	1.5	6.7	67	72
X-8C	0.103	0.0156	700^c	1.5	10.8	72	73
X-8D	0.104	0.0208	700^c	1.5	14.3	72	78
X-8E	0.103	0.0254	700^c	1.5	17.6	72	74
X-9A	0.149	0.0074	900^d	1.5	2.9	59	88
X-9B	0.149	0.0148	900^d	1.5	6.3	63	92
X-9C	0.149	0.0223	900^d	2.5	9.4	63	>100
X-9D	0.149	0.0301	900^d	2.0	15.9	79	>100
X-9E	0.132	0.0361	900^d	3.5	19.1	70	>100

[a] All reactions conducted at room temperature. [b] Determined volumetrically, 1:1 SO_3-triethyl phosphate complex. [c] 50 mL of this $CHCl_3$ was originally in the dropping funnel. [d] 100 mL of this was originally in the dropping funnel. [e] Mole percent sulfonation based on the sulfur to carbon ratio determined by elemental analysis. [f] Percent of sulfur trioxide which added to the polymer backbone. [g] Percent neutralization based on the sodium to sulfur ratio determined by elemental analysis.

excursion from the base line of the melting endotherm was taken to be the melting point (T_m). Glass transition temperatures (T_g's) were taken to be the midpoint of the step in heat capacity.

Results and Discussion

Unsaturated, Sulfonated Polypentenamers. The sulfonation of polypentenamer proceeds readily with either a 1:1 or a 2:1 complex of sulfur trioxide to triethyl phosphate. The ease with which the 1:1 complex sulfonates the unsaturated precursor makes it unnecessary to use a 2:1 complex, so the effects of this and higher complexes were not extensively examined. A summary of the reaction conditions employed and the polymers obtained is given in Table I.

It is seen from these data that the degree of sulfonation is regulated primarily by the amount of complex added to the polymer solution. The polymers prepared ranged in degree of sulfonation from 1.9 to 19.1 mol %. No attempts were made to establish the upper limit for this sulfonation reaction, since the primary interest is in polymers sulfonated below 20 mol %. In the preliminary stages of this investigation, however, while attempting to establish reaction parameters, some water-soluble sulfonated polypentenamers were prepared, indicating that sulfonation above 20 mol % without cross-linking can be achieved through this reaction.

The percent neutralization given in Table I is based on the sodium to sulfur ratio determined by elemental analysis. These values are based on the assumptions that all of the sulfur present is in the form of sulfonate groups and all of the sodium present is in the form of the sulfonate salt. Because of the manner in which these polymers are prepared, titrations such as those used to determine the percent neutralization for the thioglycolate-[3] and phosphonate-containing[4] polymers cannot be performed. Ion exchange measurements via the method developed by Fisher and Kunin[17] were considered as a means of determining the percent sulfonation but discarded on the probability that the sulfonic acid groups formed in this procedure would readily react with the unsaturated backbone of the polymer in the bulk, causing erroneous results.

The neutralization procedure used in this study results in the formation of some phosphate salts which are insoluble in alcohol but readily soluble in water. These salts can be trapped in the polymer matrix but are removed when the sulfonated polymer is washed several times with distilled water. Elemental analysis of the water-washed samples shows no trace of phosphorus.

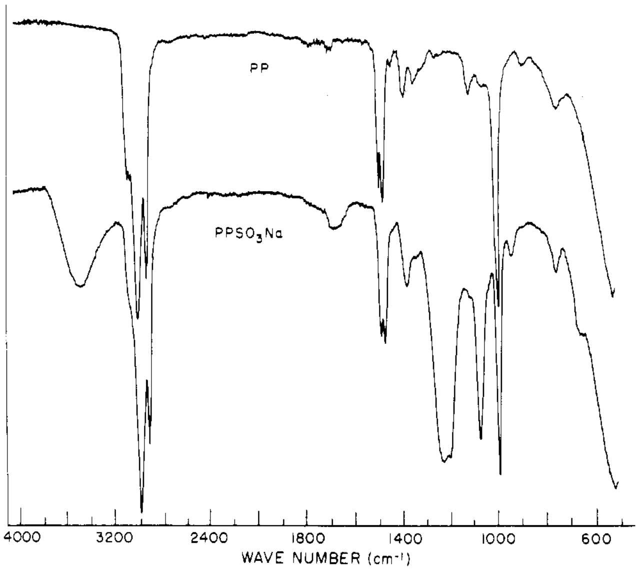


Figure 1. Infrared spectra of PP and $PPSO_3Na$.

The polymers in series X-8 were precipitated into a 0.25 M solution of NaOH in ethanol, washed with water and ethanol, stabilized, then dried, while the polymers in series X-9 were treated in a similar manner except that before stabilizing and drying they were stored overnight in a second NaOH solution and washed a second time with water and ethanol. This procedure insures the absence of phosphate salts during the second neutralization step and probably accounts for the higher degrees of neutralization obtained for the series X-9 polymers. Polymers X-9C, D, and E show a percent neutralization greater than 100 which is probably due to the fact that these samples are sulfonated above the critical concentration necessary for cluster formation.[18] As a result either low molecular weight sodium salts or excess sodium ions bound in the clusters are causing the high sodium to sulfur ratios.

Infrared Spectra Analysis. In addition to the elemental analysis results, evidence that sodium sulfonate groups have been successfully appended to the polypentenamer is found in the infrared spectra of these modified materials. Figure 1 shows the infrared spectra of the starting polypentenamer and one of its sulfonated derivatives. The sulfonated polymer shows two new and very strong absorption peaks at 1200 and 1045 cm^{-1}. The broad band centered around 1200 cm^{-1} corresponds to the O=S=O asymmetric stretch while the narrower and

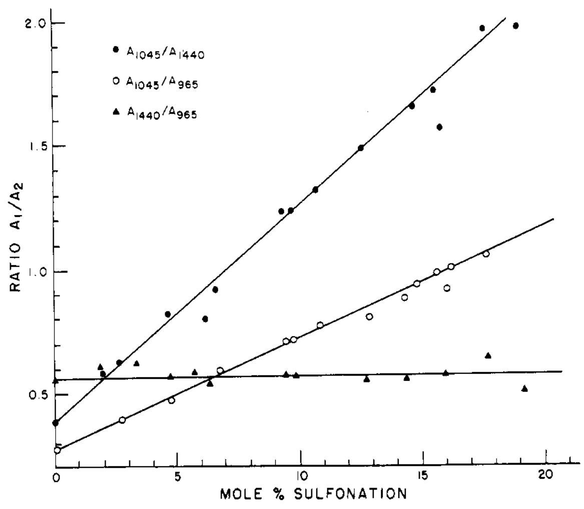


Figure 2. Ratios of the infrared peak intensities plotted against mole percent sulfonation.

slightly weaker band at 1045 cm^{-1} corresponds to the O=S=O symmetric stretch of an ionic sulfonate group.[19-21] When the ratio of the 1045-cm^{-1} absorption to the 1440-cm^{-1} absorption, which is due to backbone methylenes, is plotted against the mole percent sulfonation determined by elemental analysis, the linear correlation shown in Figure 2 is obtained. This linear relationship confirms that the sulfur being added to the polypentenamer is in the form of sulfonate groups. In addition it demonstrates that infrared spectroscopy can serve as an analytical technique for determining the degree of sulfonation.

The absorption band at 965 cm^{-1} for both the starting polypentenamer and the sulfonated derivative is due to the trans double bonds in these polymers. When the ratio of the 1045-cm^{-1} absorption to the 965-cm^{-1} absorption is plotted against mole percent sulfonation, a linear relationship is again obtained, as Figure 2 shows. The result indicates that the concentration of trans double bonds remains virtually unchanged during the sulfonation reaction.

It is also seen in Figure 2 that plotting the ratio of the 1440-cm^{-1} absorption to the 965-cm^{-1} absorption vs. the mole percent sulfonation results in a straight line of zero slope, which demonstrates that the concentration of trans double bonds does in fact stay essentially constant over the sulfonation range studied. This evidence suggests, then, that sulfonation by the SO_3/TEP complex occurs preferentially at the cis double bonds of the polypentenamer precursor.

If excess triethyl phosphate is added to the reaction mixture roughly 2 h after the initial complex is added, and if the resulting product is isolated under conditions which prevent neutralization or which allow only very incomplete neutralization, the IR spectrum of the resulting polymer displays strong peaks at 1340, 1150, and 1020 cm^{-1}. The peaks at 1340 and 1150 could be due either to sulfonate ester groups[19] or to anhydrous sulfonic acid groups.[22] In the initial work conducted by Turbak, evidence for sulfonate esters was evident for 20–40% of the material sulfonated with SO_3/TEP complexes.[13] The inability to isolate the unneutralized, sulfonated polypentenamers free from covalent cross-links, however, prevents more definitive proof of sulfonate ester groups from being obtained in these systems. In the case of sulfonate esters, the peak at 1020 cm^{-1} probably results from C–O–S linkages. Detoni and Hadzi[22] have observed a peak at 1060–1090 cm^{-1} in low molecular weight, anhydrous sulfonic acids but give little attention to its origin. Therefore it is not possible to determine whether the peaks at 1340 and 1150 cm^{-1} are due to sulfonate ester or anhydrous sulfonic acid groups on the basis of the peak at 1020 cm^{-1}.

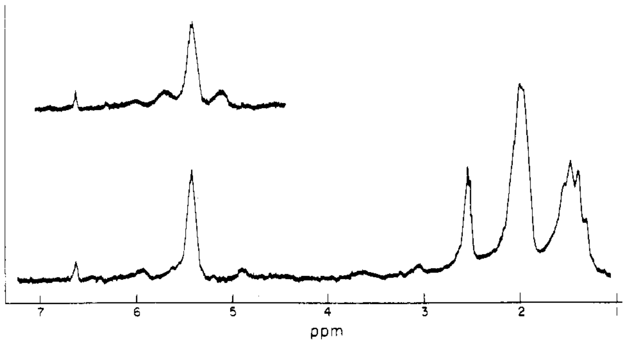
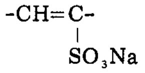


Figure 3. ^1H NMR spectrum of sample X-8E recorded at 90 °C in Me_2SO-d_6. Upper spectrum recorded at lower spin rate.

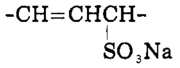
NMR Analysis. The ^1H NMR spectrum of sample X-8E is shown in Figure 3. This spectrum was recorded from a solution of the polymer in Me_2SO-d_6. From the proton spectrum of the starting polypentenamer it is known that the peaks at 1.5 and 2.0 ppm can be assigned to the backbone methylene protons, while the peak at 5.4 ppm is assigned to the protons on double bond carbon atoms. The peak at 2.5 ppm is from the deuterated Me_2SO and the small, broad band around 3.7 results from water in the system. The small peaks at 3.1, 4.8, and 6.0 ppm are side bands. This assignment is verified by changing the spinning rate as shown in the upper spectrum. The only peak which occurs in the sulfonated polymers which is not present in the starting polypentenamer is the one at 6.6 ppm.

The position of this peak permits its assignment to the proton attached to the carbon atoms in the double bond adjacent to the sulfonate group as follows

 (3)

$$\text{-CH=}\underset{\displaystyle \text{SO}_3\text{Na}}{\underset{|}{\text{C}}}\text{-} \qquad (3)$$

according to a study previously reported on several unsaturated sulfonic acids.[23] However, this proton should appear as a triplet because of the adjacent methylene group, and the spectrum displays only a slightly broadened singlet. It should be noted, however, that the absence of any peaks in this spectrum between 4.0 and 5.0 ppm means there is no NMR evidence to suggest the presence of the following structure:

 (4)

$$\text{-CH=CH}\underset{\displaystyle \text{SO}_3\text{Na}}{\underset{|}{\text{C}}}\text{H-} \qquad (4)$$

Thus while the ^1H NMR study would seem to suggest the presence of alkene sulfonate groups in the modified polymers, the results are not conclusive.

Solubility. Because the polymers prepared in this study contain ionic pendant groups, normal techniques for determining molecular weights are difficult to apply. As a result it is not clear whether or not the reaction conditions used in this study lead to chain scission. The solubility of the sulfonated polypentenamers does demonstrate, however, that the reaction conditions outlined prevent the formation of covalent cross-links. The conditions employed to dissolve these polymers are summarized in Table II. It is seen from this table that both a polar component and heat are required to overcome the ionic interactions which are present in these polymers. Samples X-8D, 8E, 9D, and 9E are also soluble in Me_2SO with only moderate heating. For the levels of sulfonation

Table II
Solubility Characteristics of Sulfonated Polypentenamers[a]

sample	% of sulfonation	wt of sample, g	solvent system[b]	temp, °C
X-8A	1.9	3.6	200 CB/100 DMF	135
X-8B	6.7	3.7	150 CB/150 DMF	135
X-8C	10.8	3.6	150 CB/150 DMF	135
X-8D	14.3	5.8	150 TCB/150 DMF	140
X-8E	17.6	12.2	100 CB/200 DMF	130
X-9A	2.9	9.5	500 TCB/200 DMF	140
X-9B	6.3	9.6	450 TCB/250 DMF	135
X-9C	9.4	9.4	350 TCB/350 DMF	135
X-9D	15.9	8.5	200 TCB/300 DMF	140
X-9E	19.1	9.7	500 DMF	130

[a] All solutions were prepared with stirring and under a steady flow of dry nitrogen. [b] Values in mL of solvent; CB = chlorobenzene, TCB = 1,2,4-trichlorobenzene, DMF = dimethylformamide.

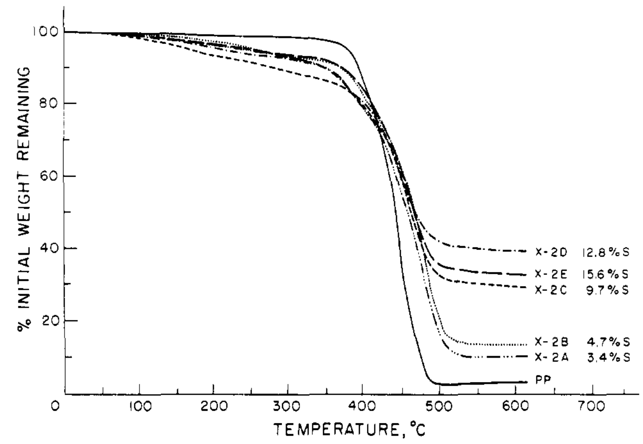


Figure 4. TGA results for unstabilized series X-2 $PPSO_3Na$ polymers.

studied, water and alcohols cause significant swelling but do not dissolve the polymers. Mixed systems of toluene or xylene with alcohols[24] did not prove to be successful solvents for these materials, although alcohols higher than butanol were not investigated.

Thermal degradation. When polymers prepared by this method are stored at room temperature under vacuum, they gradually become brittle and insoluble. When thermal gravimetric analysis (TGA) is carried out on the stored polymers, results such as those shown in Figure 4 are obtained. The most important feature of these TGA data is the large amount of residual weight present above 500 °C. The primary source of residual weight in systems of this type is either the inorganic residue of the ion-containing polymers or char formation. Table III compares the percent of residual weight found for samples in series X-2 with the weight percent of the inorganic component as determined by elemental analysis. It is evident that the inorganic component alone cannot account for all of the residual weight, indicating that a considerable portion of the remaining material is char. Since char formation often results when a polymer cross-links during thermal degradation, the presence of a significant amount of char along with the brittleness and insolubility of the stored polymers all suggest that covalent cross-links form gradually in these polymers with time.

Table III shows that for samples X-2A through X-2D, the amount of residual weight not accounted for by inorganic material increases as the degree of sulfonation increases, although sample X-2E does not fit this pattern. Sample X-2E was stored for 2 weeks less than the other samples, however. These results suggest that the cross-linking reaction which occurs is a function of both sulfur content and storage period and imply that char results not from cross-links which form during the degradation process, but rather from cross-links which form at room temperature over a period of a few weeks.

Table III
Results of Thermal Gravimetric Analysis of Unsaturated Sulfonated Polypentenamers

sample	% of sulfonation	wt % of inorganic material	% of residual wt	difference[a]
		Unstabilized		
X-2A	3.4	3.9	10	6.1
X-2B	4.7	6.4	14	7.6
X-2C	9.7	8.9	30	21.1
X-2D	12.8	11.1	41	29.9
X-2E	15.6	18.1	34	15.9
		Stabilized		
X-8A	1.9	2.7	3	0.3
X-8B	6.7	8.7	11	1.3
X-8C	10.8	13.3	13	−0.3
X-8D	14.3	16.7	16	−0.7
X-8E	17.6	18.3	18	−0.3

[a] Percent residual weight less percent inorganic material.

As mentioned above the sulfonation of olefins with the 1:1 complex of sulfur trioxide and triethyl phosphate is believed to yield alkene sulfonate groups. The presence of a carbon–carbon double bond connected to the sulfonate group most likely results in a highly reactive polymer. It is known that vinyl sulfonate polymerizes spontaneously in the absence of free radical stabilizers.[25] Thus it is reasonable to postulate that the cross-linking reaction which occurs in the sulfonated polypentenamers with aging results from a free radical mechanism involving the alkene sulfonate structure.

Such a mechanism can explain why the amount of char formation increases with the degree of sulfonation. When the free-radical stabilizer hydroquinone is incorporated into the sulfonated polypentenamer matrix, it is observed that the polymers maintain their solubility and mechanical properties even after several months of aging. The TGA results for these stabilized materials are given in Figure 5. It is seen that the amount of residual weight in the stabilized samples is much less than in the unstabilized systems.

Table III exhibits the good correlation which exists for the stabilized samples between the amount of inorganic material present and the residual weight determined by TGA. The success of hydroquinone as a stabilizer for these polymers is indicative of a free-radical mechanism for cross-link formation.

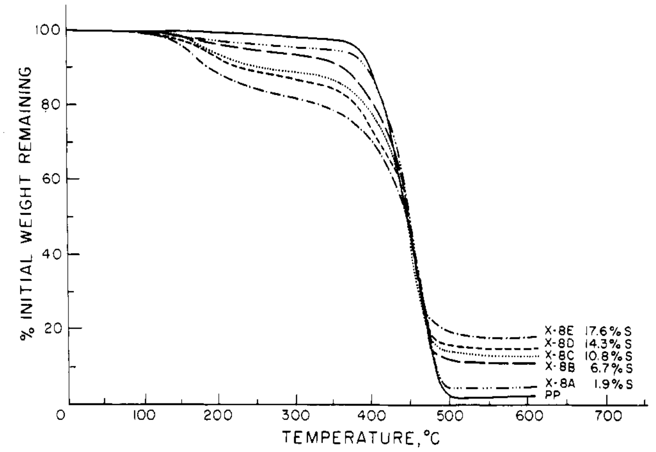


Figure 5. TGA results for series X-8 $PPSO_3Na$ polymers stabilized with hydroquinone.

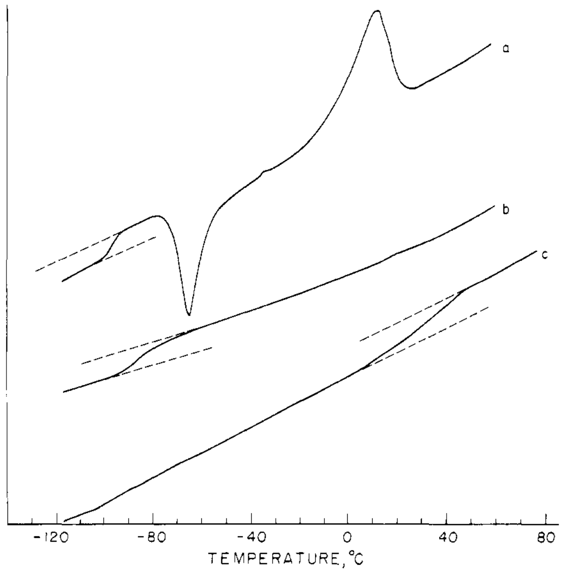


Figure 6. DSC results for samples (a) X-8A, (b) X-8B, and (c) X-8E.

The TGA scans for the stabilized sulfonated polymers also exhibit notable weight loss between 150 and 200 °C. The amount of weight loss in this region increases as the degree of sulfonation increases. It is well known that sulfonate salts of the type present in these polymers readily absorb water of hydration. The broad hydroxyl band in the IR spectrum of the sulfonated polypentenamer shown in Figure 1 suggests that these systems are no exception.[1] Data for the hydrate of sodium sulfite, $Na_2SO_3{\cdot}7H_2O$, indicate that this salt loses its water of hydration at 150 °C.[26] Because this salt is an analogue of the sodium sulfonate group pendant to the polypentenamer backbone in the polymers investigated, it is very likely that the weight loss occurring in these samples between 150 and 200 °C is caused by the loss of water of hydration. Of course $Na_2SO_3{\cdot}7H_2O$ is a crystalline, ionic salt while the sulfonated polypentenamer is an amorphous material. Therefore the analogy between the behavior of the two may be less than exact.

DSC Analysis. Figure 6 shows DSC traces for three of the polymers investigated in this study. Sample X-8A displays a well-defined glass transition at −95 °C followed by a distinct exotherm centered around −65 °C and an endotherm which peaks at 11 °C. It is known that polypentenamers containing a relatively high content of trans double bonds can exhibit a low level of crystallinity.[27,28] Thus the thermal behavior displayed by this sample can be explained as a crystallization exotherm followed by a melting endotherm with a melting point below room temperature.

Table IV
Characterization of Hydrogenated Sulfonated Polypentenamers

sample	mol % of sulfonation	% of neutralization	H/C ratio	wt % of N
HyX-9A	2.9	66	0.17	0.37
HyX-9B	6.3	84	0.17	1.02
HyX-9C	9.4	>100	0.17	1.54
HyX-9E	19.1	64	0.17	3.48

The DSC thermogram for sample X-8B, which is sulfonated to a level of 6.7 mol %, shows a distinct glass transition but no evidence for crystallization or melting. Therefore at this level of substitution the ability of the trans double bond-containing crystals to form has been disrupted. Since the sulfonation is believed to occur preferentially across the cis double bonds, however, the loss of crystallinity in this system must result from kinetic factors rather than from a disruption of the trans double bond sequences.

To demonstrate the significant change in properties which accompanies increased levels of sulfonation, the DSC scan for the 17.6 mol % sulfonated sample X-8E is also included in Figure 6. As shown in this trace, the glass transition is shifted to a significantly higher temperature and is greatly broadened. The glass transition behavior of these sulfonated polypentenamers will be examined further in a future publication.

Hydrogenated Sulfonated Polypentenamer. The previously modified polypentenamers have all been soluble in common aromatic solvents, so the hydrogenations of these polymers were carried out in *p*-xylene.[3,4] The sulfonated polypentenamers, however, are only soluble in solvent systems which contain either DMF or Me_2SO, so the hydrogenation procedure must be modified to account for this fact. As a result the hydrogenations of series X-9 polymers were carried out in the solvent systems described in Table II. After the initial hydrogenation with a 2:1 mol ratio of *p*-toluenesulfonyl hydrazide to unsaturated repeat units, the infrared spectra of the products displayed, in every case, a small amount of unsaturation remaining. Therefore, to completely eliminate unsaturated linkages, these polymers had to be hydrogenated a second time.

Table IV summarizes the characteristics of the hydrogenated sulfonated polypentenamers ($HyPPSO_3Na$). The primary feature of these results is the fact that the hydrogen to carbon ratio determined by elemental analysis is 0.17 for all four samples, which is equivalent to the theoretical hydrogen to carbon ratio for a completely hydrogenated polypentenamer. The percent neutralization decreases in these polymers compared to that found for the corresponding unhydrogenated samples. This result probably occurs because *p*-toluenesulfinic acid is one of the byproducts of the hydrogenation reaction. As a result, an equilibrium between the sulfinic acid byproduct and the sodium sulfonate groups may result in the decreased percent neutralization detected in most of these samples.

One serious drawback to this hydrogenation reaction is the presence of nitrogen in the final product. Table IV shows that the weight percent nitrogen found in the $HyPPSO_3Na$ systems increases as the percent sulfonation increases. The potential sources of nitrogen in this reaction are the solvent DMF and the *p*-toluenesulfonyl hydrazide.

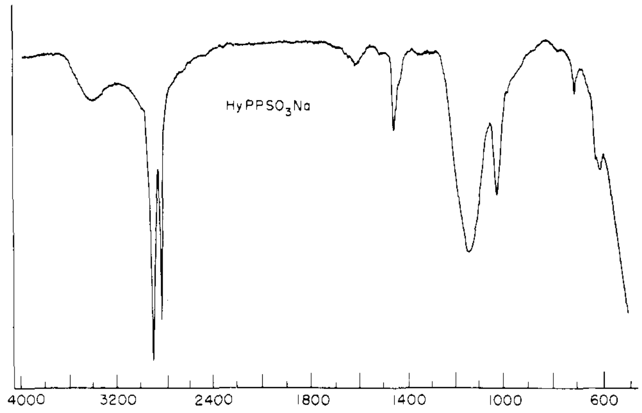


Figure 7. Infrared spectrum of $HyPPSO_3Na$.

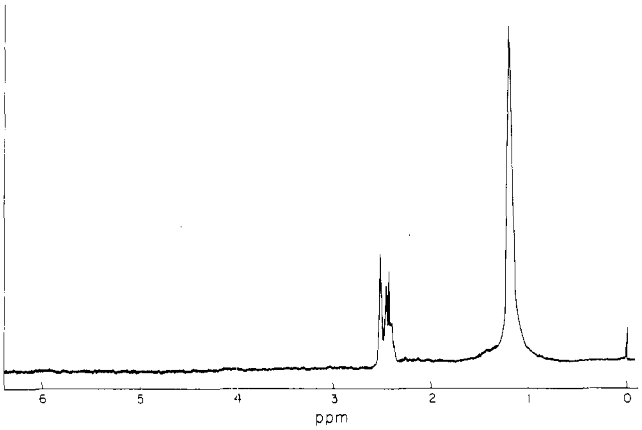


Figure 8. ^1H NMR spectrum of sample HyX-9E recorded at 90 °C in Me_2SO-d_6.

Three possible explanations for the nitrogen are: (1) some side reaction occurs between p-toluenesulfonyl hydrazide or a byproduct of the reaction and the alkene sulfonate linkage; (2) a reaction occurs between the DMF or a contaminant in the DMF and the polymer; or (3) DMF is not completely removed from the materials, but remains "bound" in the clusters. Infrared spectra and NMR give no indication of the nature of the nitrogen present.

Infrared Spectra Analysis. The disappearance of the 965-cm^{-1} band due to the trans double bonds in the infrared spectra is related to the hydrogenation of the sulfonated polypentenamers. Figure 7 shows one such spectrum. Hydrogenation also results in a slight shift of the O=S=O peaks. The asymmetric stretch band occurs at 1150 cm^{-1} for the hydrogenated polymers and the symmetric stretch band shifts to 1035 cm^{-1}. This shift is probably related to the disappearance of the double bond adjacent to the sulfonate group when these polymers are hydrogenated. The broad hydroxy peaks at 3420 and 1650 cm^{-1} illustrate that the hydrogenated polymers are hydrophilic just like their unhydrogenated precursors.

NMR Analysis. The ^1H NMR spectra of sample HyX-9E is shown in Figure 8. While this spectrum is relatively featureless, it demonstrates that the hydrogenation reaction yields a backbone which is essentially linear polyethylene. Any residual unsaturation which may be present in this polymer is below the level detectable by ^1H NMR. This spectrum was recorded in Me_2SO-d_6 which accounts for the multiplet at 2.5 ppm. Even for this most highly sulfonated sample, the level of sulfonation is too low for the protons α to the sulfonate groups to be observed. The fact that these protons would be split into a quintet also makes their detection difficult.

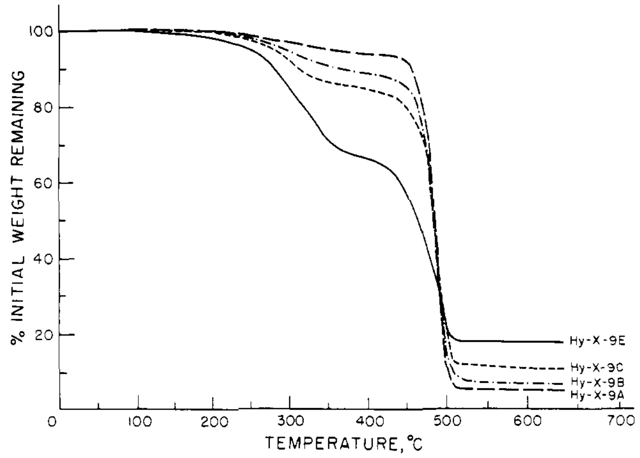


Figure 9. TGA results for series HyX-9 polymers.

Table V
Results of Thermal Gravimetric Analysis of Hydrogenated Sulfonated Polypentenamers

sample	wt % of inorg material	% of residual wt
HyX-9A	3.6	5
HyX-9B	7.8	8
HyX-9C	11.5	11
HyX-9E	17.3	18

Table VI
DSC Results for Hydrogenated Sulfonated Polypentenamers

sample	thermal history[a]	wt % of crystallinity	T_m, °C
HyX-9A	A	54	127
	Q	47	122
HyX-9B	A	52	120
	Q	37	120
HyX-9C	A	34	115
	Q	22	107
HyX-9E	A	13	96
	Q	9	97

[a] A = annealed for 3 days at 80 °C. Q = quenched immediately in a dry ice-isopropyl alcohol bath.

Thermal Degradation. The TGA scans for the $HyPPSO_3Na$ materials are shown in Figure 9. These polymers show the onset of decomposition between 150 and 200 °C, as did the unsaturated polymers. However, while the unsaturated polymers show some weight loss between 150 and 200 °C followed by stability up to approximately 350 °C, the hydrogenated materials show continued weight loss from 150 to 350 °C, followed by a slight plateau and then major decomposition. It is seen that the amount of weight lost below 350 °C increases as the degree of sulfonation increases. While some of this initial weight loss probably is due to the loss of water, it is apparent that the addition of sulfonate groups to the polyethylene-like backbone of the hydrogenated polypentenamer greatly reduces its thermal stability.

A comparison of the residual weight after decomposition to the amount of the inorganic component present in the $HyPPSO_3Na$ polymers is made in Table V. As in the case with the stabilized, unsaturated systems, the correlation is quite good. The fact that the hydrogenated materials do not require the hydroquinone stabilizer to avoid cross-linking is further evidence that the cross-linking which does take place in the unsaturated systems occurs through the carbon-carbon double bonds adjacent to the sulfonate groups.

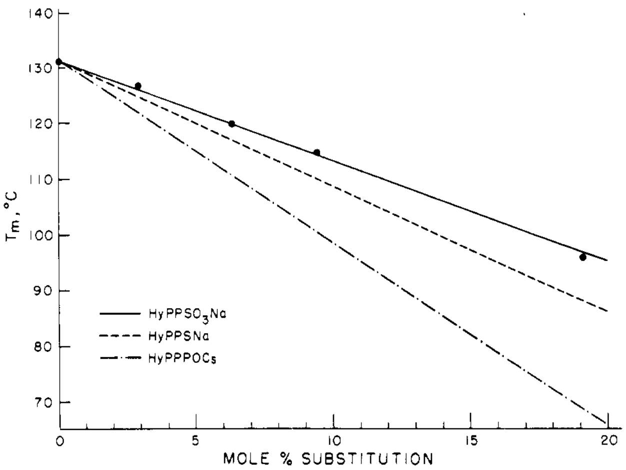


Figure 10. Melting point vs. mole percent substitution for hydrogenated polypentenamers bearing sulfonate, thioglycolate, and phosphonate groups.

DSC Analysis. Evaluation of the hydrogenated derivatives by DSC yields some interesting features. Table VI summarizes the crystallinities and melting points determined for these polymers. Crystallinity values are based on the ratio of $\Delta H_f/\Delta H_u$ where ΔH_f is the experimental enthalpy of fusion and ΔH_u is the enthalpy of fusion for the hypothetical 100% crystalline polymer. Because the sulfonate groups are assumed to be completely excluded from the crystalline phase in these polymers, the ΔH_u value of 59 cal/g determined for fully hydrogenated polypentenamer by the polymer–diluent technique was used.[1] As would be expected the degree of crystallinity decreases as the percent sulfonation increases.

The DSC scans of the HyPPSO$_3$Na polymers are unusual in that two melting endotherms are observed for all of the polymers, and the magnitude of the low-temperature endotherm increases both as a function of sulfonate concentration and time maintained at room temperature. Such behavior has previously been observed in poly(ethylene-*co*-methacrylic acid) ionomers[29] where the low temperature melting phenomenon was believed to be due to short, imperfect polyethylene crystallites which form on annealing at room temperature. This behavior will be examined more fully in a future publication.

Although these polymers display two melting endotherms, the temperature of the low-melting peak remains constant while the higher melting point is observed to decrease as the degree of sulfonation increases. Figure 10 illustrates the melting point depression which accompanies sulfonation for annealed films and gives a comparison of this melting point depression to that observed for thioglycolate and phosphonate substituted polypentenamers in the hydrogenated form. The slopes of the lines representing the dependence of T_m on pendant group concentration are −3.4 deg/mol % for the phosphorylated materials, −2.2 deg/mol % for the thioglycolate substituted systems, and only −2.0 deg/mol % for the sulfonated samples. It would appear, therefore, that the sulfonate groups have the smallest disruptive effect on the polyethylene crystal lattice of the three systems investigated, but no explanation of this fact is readily apparent.

Random Placement of Sulfonate Groups. Polypentenamers are known to have a very regular repeating structure of three methylenes between subsequent double bonds;[30,31] however, the distribution of cis and trans sequences can be either random or somewhat blocky.[32,33] Since the sulfonation reaction is believed to occur preferentially on cis bonds, a random distribution of the cis bonds in the precursor should lead to a random placement of the pendant sulfonate groups. Instrumental limitations have precluded the acquisition of ^{13}C NMR spectra of sufficient resolution to determine cis–trans sequencing in the precursor used in this study. The melting point of the trans double bond containing crystals present in the starting material[34] and the knowledge that polypentenamers of this particular trans content have generally been observed to display random cis–trans placement,[32] however, both suggest that the cis bonds are randomly distributed in the precursor employed. Verification awaits study by higher resolution ^{13}C NMR.

The crystallinity and melting point behavior of the hydrogenated derivatives suggests that the pendant groups are randomly spaced. As the degree of sulfonation is increased, the degree of crystallinity is seen to decrease in a regular manner. More importantly, however, the melting point displays a linear depression when plotted against the mole percent sulfonation. Such behavior is indicative of random placement of the sulfonate groups.

Conclusions

A technique has been developed to sulfonate polypentenamers to a significant level while avoiding the formation of covalent cross-links. The sulfonation is believed to occur preferentially across the cis double bonds to provide for random placement of the pendant groups. These polymers cross-link on storage if not stabilized. The sulfonated polymers can be readily hydrogenated to give semicrystalline sulfonated polyethylenes which are stable to cross-linking even in the absence of added stabilizers. Both the unsaturated and the hydrogenated polymers are hydrophilic and both exhibit interesting thermal behavior.

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The Mannich Reaction of Poly(acrylamide)

C. J. McDonald* and R. H. Beaver

Michigan Division, Dow Chemical Corporation, Midland, Michigan 48640.
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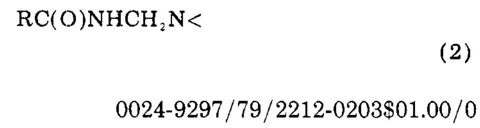
ABSTRACT: The Mannich reaction of formaldehyde and dimethylamine with a polymeric substrate, poly(acrylamide), was studied with carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR). Reaction rates, equilibria, and the mechanism of conversion are characterized for the base-catalyzed reaction. The formation of the Mannich derivative is best described as a second-order process, involving the polymer and (dimethylamino)methanol, a rapidly formed product of dimethylamine and formaldehyde. The reaction exhibits a reversible equilibrium evidenced by a decrease in Mannich conversion with a molar excess of amine. A model equation describing this behavior gave estimates for the major equilibrium constants. Rate data, obtained in the absence of (dimethylamino)methanol, indicated that the reaction of the polymer with *N,N,N′,N′*-tetramethyldiaminomethane does not play a prominent role in the kinetics.

The Mannich reaction has been studied extensively and applied in the development of a wide range of compounds having commercial and synthetic importance.[1-4] This reaction involves the condensation of an amine, an aldehyde, usually formaldehyde, and a compound having a labile proton. The mechanism and reactive intermediates have been investigated, leading to some generalized conclusions. For example, it is now well accepted that the reaction normally involves the condensation of the *N*-hydroxymethylamine or methylenediamine with the labile hydrogen compound under both acidic and basic conditions.[3-7]

This study will describe the base-catalyzed Mannich reaction of dimethylamine and formaldehyde with a polymeric amide, poly(acrylamide). Direct spectroscopic

$$[\text{-CH}_2\text{CH(C=O)NH}_2\text{-}]_n \xrightleftharpoons[\text{CH}_2(\text{OH})_2]{(\text{CH}_3)_2\text{NH}} [\text{-CH}_2\text{CH(C=O)NHCH}_2\text{N(CH}_3)_2\text{-}]_n + 2\text{H}_2\text{O} \quad (1)$$

analysis of the reactions, primarily by carbon magnetic resonance[8,9] (^{13}C NMR), has permitted a close examination of the kinetics of the transformation and the reaction equilibria and has confirmed the synthesis route as



$$2\text{CH}_2(\text{OH})_2 + 3{>}\text{N-H} \rightleftharpoons {>}\text{NCH}_2\text{OH} + {>}\text{NCH}_2\text{N}{<} + 3\text{H}_2\text{O};\quad {>}\text{NCH}_2\text{OH} \xrightarrow{\text{RC(O)NH}_2} \text{RC(O)NHCH}_2\text{N}{<} \quad (2)$$

Table I
Polymer Characterization

	wt av mol wt
viscosity equation[12]	9.7×10^4
light scattering[a]	8.4×10^4

[a] Light scattering data, 628 nm; distilled water: 25 °C; $dn/dc = 0.182$.

Experimental Section

I. Polymer Synthesis. Poly(acrylamide) was prepared by a free radical solution polymerization initiated by the redox pair, sodium bisulfite–sodium persulfate. Initiator components were introduced simultaneously into a 20% nitrogen purged aqueous solution of Dow's acrylamide monomer. After the exotherm subsided the polymer was heated to 100 °C and allowed to cool slowly to ambient temperature to minimize unreacted monomer. The level of unsaturation left in the system was measured at less than 0.15% as determined by the bromate–bromide titration method.[10,11] The molecular weight, controlled by initiator level, was maintained below 100 000 to enable working with a low viscosity solution of the polymer derivative having greater than 20 wt % solids. The weight average molecular weight was measured by light scattering and with a viscosity equation.[12] These data are listed in Table I.

II. NMR Data. A. 25 MHz ^{13}C NMR Data. Fourier transform ^{13}C NMR were obtained at 25.2 MHz using a Varian XL-100 NMR spectrometer equipped with a Digilab FTS/NMR3 data system and a Varian V-6040 variable temperature controller. During operation, the spectrometer was locked on an external ^{19}F signal (C_6F_6). Protons were decoupled with broad band radio frequency noise.

Repetitive 30° (8 μs) pulses applied at 250 Hz to the low frequency of Me_4Si were used to generate the carbon-13 free induction signals, which were filtered (15 kHz single side band crystal, 6.2 kHz RC, and 12 kHz Butterworth), digitized at a rate of 10 560 points/s (5280 Hz bandwidth), and accumulated in

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