Macromolecules **1989**, *22*, 1058–1064

Ceric Ion Initiation of Vinylidene Chloride from Poly(vinyl alcohol)

Robson F. Storey* and Leslie J. Goff[†]

Department of Polymer Science, University of Southern Mississippi,
Southern Station Box 10076, Hattiesburg, Mississippi 39406-0076. *Received May 19, 1988; Revised Manuscript Received August 2, 1988*

ABSTRACT: The mechanism of ceric ion induced free radical formation on the poly(vinyl alcohol) (PVOH) backbone was studied with and without the presence of vinylidene chloride (VDC) monomer. The grafting of VDC from PVOH was carried out at various concentrations of PVOH and constant Ce^{IV} concentration. Differences in the copolymer products from these reactions are discussed in terms of the possible initiation sites along the PVOH backbone. Ce^{IV} oxidizes PVOH most rapidly at 1,2-diols inherent in PVOH. This reaction causes cleavage of the PVOH backbone and produces a block copolymer segment rather than a true graft. Exhaustive oxidation of the 1,2-diols in the subject PVOH sample, using either Ce^{IV} or periodic acid in the absence of VDC, showed the PVOH contains 1.9 mol % 1,2-diols. The resulting diol-free PVOH, when reacted with Ce^{IV} under conditions of $[Ce^{IV}]/[OH] \ll 1$, yielded a pseudo-first-order rate constant of 0.040 min^{-1} at 40 °C. The redox reaction between Ce^{IV} and 1,2-diols was examined by monitoring the Ce^{IV} concentration and the PVOH molecular weight under conditions of low Ce^{IV} concentration. The Ce^{IV}/1,2-diol stoichiometry was found to vary with temperature, i.e., from 2.0 at 0 °C to 1.5 at 30 °C. Within this temperature range a pseudo-first-order rate constant for reaction of Ce^{IV} with 1,2-diols was measured with a temperature dependence defined by $k = 6.1 \times 10^{12} \exp(-18.3 \text{ kcal}/RT)$ min^{-1}.

Introduction

Incorporation of vinylidene chloride (VDC) into coatings polymers may potentially improve such important properties as oxygen and water transmission, fire retardancy, gloss, and oil and solvent resistance. Aqueous ceric ion grafting is a particularly attractive route of incorporation of VDC due to the ever-increasing interest in water-borne paint and coatings. If an initially water soluble backbone polymer is chosen, it appears possible to produce a self-stabilized, aqueous suspension of graft copolymer product which forms a water-impervious film upon drying. In a previous paper[1] we described the grafting of VDC from poly(vinyl alcohol) (PVOH). We found that the incidence of homopolymer formation was very low, and we established conditions under which percent weight gain due to grafting could be optimized. This work clearly showed that homopolymer formation during ceric ion grafting is very low for systems in which the substrate, in this case PVOH, is by far the strongest reducing agent in the polymerization mixture. Strongly contrasting behavior has been observed in graft polymerizations of acrylamide,[2] where oxidation of the monomer itself brings about homopolymer formation.

Oxidation of PVOH by Ce^{IV}, with[3-6] and without[7] the presence of polymerizable monomers, has been actively studied over the years. It is generally accepted that Ce^{IV} forms radical on the PVOH substrate most readily by oxidation of 1,2-diol units, i.e., vicinal hydroxyl groups, which occur as a result of occasional head-to-head monomer incorporation during polymerization of vinyl acetate.[8,9] Head-to-head linkages in PVOH are reported to occur to the extent of 1–2 mol % along the backbone.[10] Mino et al.,[7] by reacting Ce^{IV} with PVOH which had been freed of 1,2-diols, conclusively proved that isolated hydroxyl groups, derived from normal head-to-tail monomer addition, were also oxidized by Ce^{IV}, but at a much slower rate.

Early work by Flory and Leutner[8] demonstrated that exhaustive periodic acid oxidation of the 1,2-diols in PVOH caused cleavage of the C–C bonds which connect the vicinal hydroxyl groups. The number-average molecular weight of the PVOH after degradation, M_n, was used to characterize the mole fraction 1,2-diol content, Δ, through the equation

$$\Delta = M_0(1/M_n - 1/M_{n0}) \qquad (1)$$

where M_{n0} is the number average molecular weight before degradation, and for PVOH, $M_0 = 44$ g/mol. Equation 1 is generally useful for any oxidation process which cleaves the 1,2-diols of PVOH, including Ce^{IV} oxidations. For a nonexhaustive degradation, Δ becomes simply the mole fraction repeat units which were cleaved to lower the molecular weight from M_{n0} to M_n.

It has been known for many years that Ce^{IV} leads to C–C bond cleavage at 1,2-diol structures. Mino et al.[11] demonstrated that pinacol was cleaved at the 1,2-diol by Ce^{IV}, and the resulting free radicals were capable of initiating vinyl polymerization. Hintz and Johnson[12] studied the oxidation of cyclic alcohols and cyclic 1,2-diols by Ce^{IV} and found that C–C bond cleavage occurred only with the 1,2-diols. For example, cyclohexanol yielded cyclohexanone as a near quantitative oxidation product, while both *cis*- and *trans*-1,2-cyclohexanediol yielded >90% adipaldehyde.

Ogiwara and Uchiyama[5] examined the kinetics of reduction of Ce^{IV} by PVOH. They suggested the progress of Ce^{IV} reduction can be dividied into three stages, each stage displaying a different rate of reduction. The initial stage is a very rapid reduction of Ce^{IV} which was attributed to oxidation of 1,2-diol units. This is followed by a second stage of slower rate, and a third stage of very slow rate. The authors observed chain cleavage of the PVOH during stage one, and they showed that the majority of grafting occurred during stage one as a result of oxidation of 1,2-diols. From these results the authors concluded that the copolymer product was principally a block copolymer.

Iwakura and Imai[4] and Mino et al.[7] also suggested the formation of block copolymers during ceric ion induced grafting from PVOH. However, Mino et al.[7] argued that only under conditions of a very large excess of PVOH, i.e., $[1,2\text{-diol}]/[Ce^{IV}] > 10$, would radicals be produced only at the ends of the fragmented PVOH, leading to block copolymers. Under normal grafting conditions, a mixture of block and graft copolymers would be expected.

Early investigations by Duke and co-workers[13,14] concerning the mechanism of oxidation of 1,2-diols by ceric

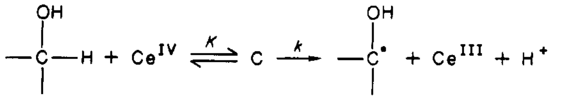
---

[†] Current address: Plastics Technology Division, General Electric Company, Highway 69 South, Mt. Vernon, IN 47620.

0024-9297/89/2222-1058$01.50/0

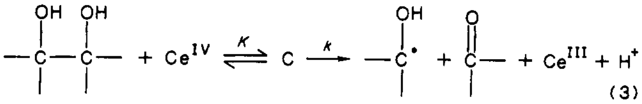
ion led to the general acceptance of the intermediacy of a coordination complex between Ce^{IV} and oxidizable diols. Monoalcohols such as methanol, ethanol, and 2-propanol are also believed to form complexes with Ce^{IV} and to be oxidized in a similar manner.[7] In fact, the use of such complexes for the qualitative colorimetric determination of alcohols was advanced very early by Duke.[15] The complexes have been shown to be rapidly established in an acidic aqueous medium and are readily observed by using UV/visible spectroscopy.[16] Although Ce^{IV} has a coordination number of six and could thus conceivably coordinate with six monoalcohols or three 1,2-diols,[13,14] it has been demonstrated that the complexes involve one molecule of diol (or monoalcohol) and one Ce^{IV} [12,16] and that the ceric ion complex with a diol is a chelated complex.

According to the well-accepted mechanism,[7,12-14] the rate-determining step of the oxidation is the unimolecular disproportionation of the complex C to yield cerous ion, a proton, and a free radical on the alcohol substrate:



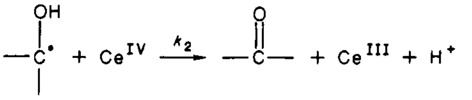
$$-\overset{\text{OH}}{\underset{|}{\overset{|}{\text{C}}}}-\text{H} + \text{Ce}^{\text{IV}} \overset{K}{\rightleftharpoons} \text{C} \xrightarrow{k} -\overset{\text{OH}}{\underset{|}{\overset{|}{\text{C}}}}{}^{\bullet} + \text{Ce}^{\text{III}} + \text{H}^{+} \qquad (2)$$

If the alcohol is a 1,2-diol, the carbon–carbon bond between the hydroxyls cleaves to yield an aldehyde or ketone and a free radical:



$$-\overset{\text{OH}}{\underset{|}{\overset{|}{\text{C}}}}-\overset{\text{OH}}{\underset{|}{\overset{|}{\text{C}}}}- + \text{Ce}^{\text{IV}} \overset{K}{\rightleftharpoons} \text{C} \xrightarrow{k} -\overset{\text{OH}}{\underset{|}{\overset{|}{\text{C}}}}{}^{\bullet} + \overset{\text{O}}{\underset{|}{\overset{\|}{\text{C}}}}- + \text{Ce}^{\text{III}} + \text{H}^{+} \qquad (3)$$

The fate of the free radical in both cases is supposedly a fast oxidation by another ceric ion:



$$-\overset{\text{OH}}{\underset{|}{\overset{|}{\text{C}}}}{}^{\bullet} + \text{Ce}^{\text{IV}} \xrightarrow{k_2} -\overset{\text{O}}{\overset{\|}{\text{C}}}- + \text{Ce}^{\text{III}} + \text{H}^{+} \qquad (4)$$

The ceric ion induced grafting from PVOH thus emerges as a complex process in which vinyl polymerization of grafted chains occurs simultaneously with degradation of the PVOH backbone. Oxidation of 1,2-diols and isolated hydroxyls both occur, but the former is much the faster reaction. Oxidation of 1,2-diols cleaves the PVOH chain and yields a radical at the fragment end. Thus the graft copolymer product is best viewed as a mixture of block and graft copolymers.

In an earlier paper[1] we described ceric ion initiated grafting reactions of VDC from PVOH. The reaction is heterogeneous, consisting of an acidic aqueous phase containing Ce^{IV} and PVOH and an organic phase consisting of VDC monomer. The product is a suspension of PVDC/PVOH block and graft copolymer in an aqueous medium.

This paper describes a detailed kinetic investigation of our polymerization system, undertaken to better define the nature of the initiation reaction and to understand the role of the various alcohol structures during graft initiation. Studies were carried out on both virgin PVOH and PVOH which had been freed of 1,2-diol units (diol-free PVOH). The rate of consumption of Ce^{IV} was monitored by titration, and the M_n of the PVOH was monitored during oxidation to characterize the extent of 1,2-diol cleavage, using eq 1, which had occured at any time during the reaction.

Experimental Section

Materials. PVOH (Air Products) of M_n = 74 000 was 96% hydrolyzed according to the manufacturer. It was purified by dissolving in reverse osmosis (RO) water at 90 °C and precipitating into reagent grade acetone. VDC (Dow Chemical) was washed with 5% NaOH, washed with water, and dried over magnesium sulfate. It was then vacuum distilled such that the temperature of the monomer never exceeded 26 °C. Ceric ammonium nitrate (CAN) (Fisher Scientific) was used as received. A standard solution of 0.156 M CAN in 0.1 N HNO_3 was prepared for grafting reactions. All other chemicals were reagent grade and used as received.

Preparation of Diol-Free PVOH. Approximately 7.5 g of PVOH (M_n = 74 000) was dissolved in 100 mL of RO water and charged into a three-neck flask. A 10% solution of H_5IO_6 (periodic acid) (Fisher Scientific) was prepared by using RO water, and 10 mL of this solution was charged to the PVOH solution while stirring. Stirring was continued for 60 min under CO_2. The polymer was precipitated in excess acetone and collected by filtration. The polymer was then dissolved in 100 mL of RO water and allowed to stir with 20 mL of a 2% solution of sodium borohydride (Fisher Scientific) prepared from 1 N NaOH. After 15 min the pH of the mixture was adjusted to 1.0 with 0.1 N HCl. The polymer was precipitated in excess acetone and dried in a vacuum oven at room temperature. Finally, the polymer was extracted in a Soxhlet extractor using a water–2-propanol azeotrope for 100 h to remove borohydrides.

Graft Polymerization. In a typical graft polymerization, 20 mL of an aqueous PVOH solution of appropriate concentration was charged into a chilled (0 °C) glass ampule. Then, to the ampule were added, prechilled, 0.1 N nitric acid solution (2.0 mL), 2.4 g of VDC, and 0.156 M CAN solution (2.0 mL). This produced a two-phase reacting system with a 23-mL aqueous phase suspended over ~2 mL of VDC. The ampule was subjected to three freeze–pump–thaw cycles and sealed under vacuum. The reaction was carried out at 40 °C for 3 h, during which each ampule was agitated every 20 min. The products were precipitated in methanol, collected by filtration, and dried to constant weight.

Oxidation of PVOH (Method I—Data for Figure 3 Only). A number of ampules were charged with 10 mL of a 20 g/L aqueous solution of PVOH. Nitrogen was bubbled through each ampule for 30 min, and then 0.5 ml of 0.156 M CAN solution was charged to each ampule. The ampules were sealed and placed into a 40.0 °C water bath and reacted for varying times. The reactions were stopped by pouring the contents of each ampule into excess methanol. The polymers were precipitated again in acetone and dried in a vacuum oven overnight at room temperature.

Oxidation of PVOH (Method II—Including Determination of Ce^{IV} Concentration). Into a three-neck flask was charged 100 mL of a 22 g/L aqueous solution of PVOH. While stirring, 10 mL of 1 N sodium nitrate (Aldrich Chemical) was added. The system was purged with nitrogen and equilibrated to the desired reaction temperature. The 0.156 M CAN solution was equilibrated to the reaction temperature and injected (5 mL) into the reaction vessel to yield $[Ce^{IV}]$ = 6.8 mmol/L. The reaction was allowed to proceed under a nitrogen blanket. Samples were withdrawn at recorded times and quenched in an excess of 0.05 N ferrous ammonium sulfate (Fisher Scientific) solution in 0.5 N sulfuric acid. The excess ferrous salt was titrated with 0.05 N ceric sulfate (Aldrich Chemical), using *o*-phenanthroline indicator. The ferrous salt solution was standardized before use with 0.05 N potassium permanganate (Aldrich Chemical), and the ceric sulfate solution was standardized with the ferrous salt solution.

For pseudo-first-order reactions the ceric ion concentration was 0.34 mmol/L. The same procedure was employed with appropriate adjustments in titrant concentrations.

Molecular Weight Determinations. Molecular weight determinations were performed by using a Knauer membrane (MO) and vapor pressure osmometer (VPO).

Results and Discussion

Characteristics of PVDC Grafting from PVOH. In our initial paper describing VDC grafting from PVOH,[1] we indicated that the percent weight gain due to grafting (% wt gain = (wt of graft product − wt of PVOH)/wt of PVOH) increases with an increase in PVOH concentration at a constant concentration of ceric ion. We have since performed more extensive investigations covering a broader

Table I
Ceric Ion Grafting of VDC from PVOH

run	[PVOH],[a] g/L	wt gain, %	run	[PVOH],[a] g/L	wt gain, %
1	17.4	65	7	9.6	118
2	14.8	85	8	7.8	89
3	13.0	60	9	6.1	136
4	13.0	70	10	3.5	263
5	12.2	114	11	1.7	250
6	10.4	117			

temp = 40.0 °C
reactn time = 3 h
VDC = 2.4 g (2.0 mL)
$[Ce^{IV}]^a$ = 6.8 mmol/L

[a] Concentrations are based on 23-mL aqueous volume. Total reaction volume including monomer ≅ 25 mL.

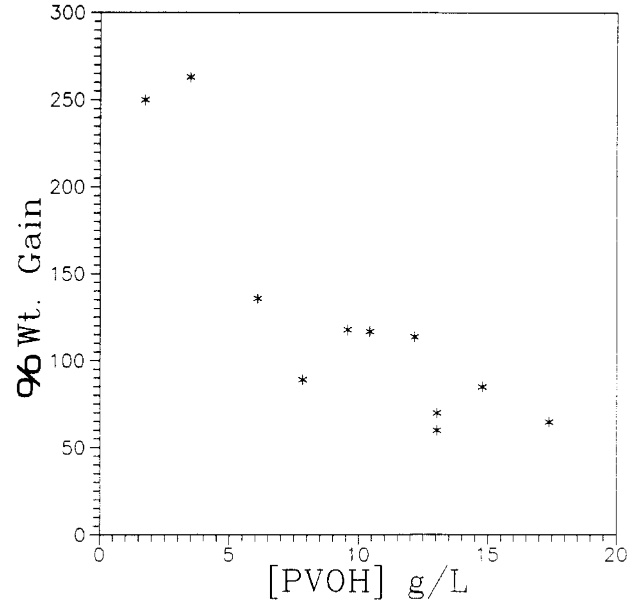


Figure 1. Percent weight gain during grafting of VDC from PVOH, as a function of [PVOH] at constant initial $[Ce^{IV}]$ = 6.8 mmol/L (concentrations based on 23 ml aqueous volume). Temperature = 40.0 °C. Reaction time = 3 h. VDC charge = 2.4 g.

range of PVOH concentrations, and we have found that, in fact, percent weight gain is relatively constant within the narrow range of conditions reported earlier but increases dramatically at very low [PVOH]. Table I and Figure 1 outline the results.

There was a noticeable difference in the appearance of the graft product formed at low concentrations of PVOH. At [PVOH] < 4.0 g/L and $[Ce^{IV}]$ = 6.8 mmol/L, a hard precipitate settled from the aqueous layer, which, when filtered and dried, formed a powder. Higher concentrations of PVOH (5.0 g/L and higher) yielded stable suspensions of copolymer product, which upon removal of water formed films.

It was of interest to determine the extent of homopolymer formation, if any, under these varius reaction conditions. The powdery product obtained from 4.0 g/L PVOH and 6.8 mmol/L Ce^{IV} (which is approximately 4 times the ceric ion concentration for normal grafting reactions) was extracted for 24 h at 90 °C with RO water and 24 h at 70 °C with *N*-methylpyrrolidone in a Soxhlet extractor. In neither case was PVOH or PVDC homopolymer extracted from the graft copolymer product.

As discussed earlier, the PVOH/Ce^{IV} system is complicated by the existence of two types of oxidizable hydroxyls. One type is the isolated hydroxyl which results from normal head-to-tail addition of vinyl acetate and represents over 98% of the hydroxylic sites along the PVOH backbone. The other type of oxidizable hydroxyl is the 1,2-diol produced by occasional head-to-head addition of vinyl acetate monomer. It is known that Ce^{IV} has a 60–70 times greater propensity to bind with 1,2-diols than with isolated hydroxyls.[12,16] However, due to the overwhelmingly greater number of isolated hydroxyls, inherent in this system is the competition for Ce^{IV} between these two types of oxidizable functions.

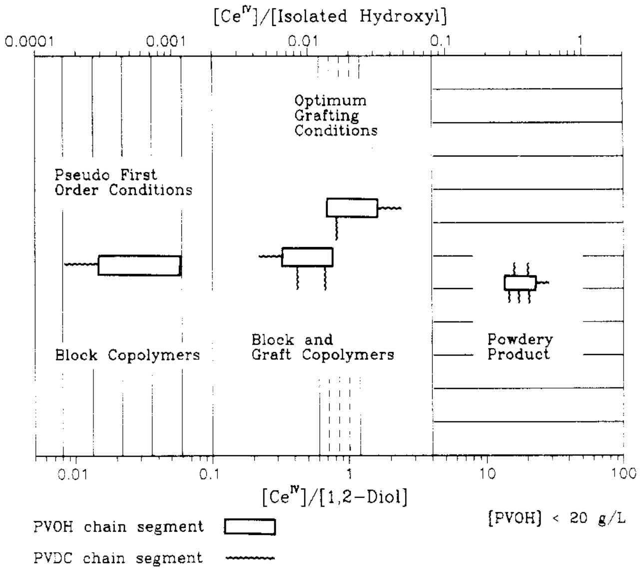
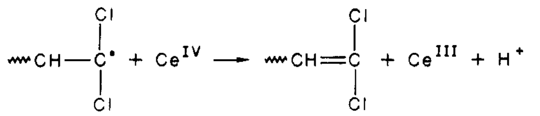


Figure 2. Schematic representation of block and graft copolymer products obtained over a broad range of Ce^{IV}/PVOH reactant ratios.

In comparing the different graft products it is obvious that the $[Ce^{IV}]$/[PVOH] ratio has a pronounced effect on the molecular structure of the copolymer product. As this ratio is varied over a wide range, it is convenient to divide experimental conditions into two categories based on visual observations of the product. On the one hand are systems that employ a high Ce^{IV}/PVOH ratio (> 1.5 mmol of Ce^{IV}/g of PVOH) and produce a powdery product; the other are systems with lower Ce^{IV}/PVOH ratios that produce film-forming copolymers.

It is proposed that in the high Ce^{IV}/PVOH systems the ceric ion is in such great abundance that it oxidatively cleaves all of the 1,2-diols. This reduces the PVOH segments to their minimum possible M_n, which is determined by the original mol % of 1,2-diols in the backbone. Since the concentration of Ce^{IV} is typically 10 times the 1,2-diol concentration under these conditions, there remains plenty of ceric ion to form complexes with isolated hydroxyls, which in turn produce grafted side chains rather than blocks. Thus, the powdery product is viewed as a short segment of PVOH with many grafted chains and possibly a block of PVDC originating from the terminal radical produced from cleavage of a 1,2-diol. Figure 2 depicts schematically the nature of the copolymer product to be expected at various $[Ce^{IV}]$/[1,2-diol] ratios.

Ceric ion is reported to be also involved in termination of growing chains.[17,18]



$$\sim CH-\overset{Cl}{\underset{Cl}{C^{\bullet}}} + Ce^{IV} \longrightarrow \sim CH=\overset{Cl}{\underset{Cl}{C}} + Ce^{III} + H^{+} \quad (5)$$

With excess Ce^{IV} there is more opportunity for earlier termination, which would decrease the length of grafted chains.

For low Ce^{IV}/PVOH systems, which includes optimum grafting conditions as determined by our previous work[1] (shown as a narrow, shaded band in Figure 2), the $[Ce^{IV}]/[1,2\text{-diol}]$ ratio is approximately 1:1. Since reaction of Ce^{IV} is faster with 1,2-diols, this system is thought to produce predominantly block copolymers with a lesser percentage of grafted chains. As the $[Ce^{IV}]/[1,2\text{-diol}]$ ratio is decreased further (moving to the left in Figure 2), the small ceric ion population reacts almost exclusively with 1,2-diols, producing solely block copolymers. Since 1,2-diols are in large excess, one also obtains pseudo-first-order kinetics with respect to Ce^{IV}.

The difference in physical properties of these two systems may be rationalized in terms of the number of grafted or block segments and by their relative length. The high $[Ce^{IV}]/[PVOH]$ system (system 1) produces more but shorter chains of PVDC. The lower $[Ce^{IV}]/[PVOH]$ system (system 2) produces fewer but longer PVDC chains, which in fact are predominantly block, resulting in considerably less branching. With less cleavage of the PVOH chain in system 2, the PVOH segments theoretically would be larger.

The block and graft copolymer produced in system 2 formed slightly yellow, brittle films. Film formation may be attributed to fewer attached segments of PVDC, reducing the tendency for extensive PVDC crystallization. Copolymers produced in system 1 displayed properties very similar to PVDC homopolymer, indicating high crystallinity. In fact, as Figure 1 shows, copolymers produced at low [PVOH] are, by weight, predominantly PVDC. It was also observed that precipitation or phase separation (formation of suspension) occurred earlier in system 1 than in system 2. This would also suggest higher PVDC content and higher crystallinity in system 1.

Oxidations of PVOH in the Absence of Monomer. The M_n of the unoxidized PVOH was determined to be 74 000 by MO. Periodic acid was used to cleave the PVOH chain at each 1,2-diol group to produce a diol-free PVOH. After reaction, the M_n of the diol-free PVOH was found by VPO to be 2200. When a similar oxidation was carried out by using Ce^{IV}, the M_n of the PVOH was also found to be 2200.

This result indicates that Ce^{IV} oxidation of PVOH, which leads to chain cleavage, occurs exclusively and quantitatively at the 1,2-diol structures. Although oxidation of isolated hydroxyls also occurs, it does not lead to chain cleavage. On the basis of these results, the mole percent 1,2-diol groups, Δ, in the subject PVOH was calculated to be 1.9% using eq 1 given by Flory and Leutner.[8] This agrees well with Mino et al.,[11] who found $\Delta = 1.4\%$ for PVOH prepared in their laboratory.

The kinetics of 1,2-diol oxidation by Ce^{IV} was monitored by observing the resulting decrease in M_n. The first set of conditions examined were typical of those used for efficient grafting, i.e., 40 °C, with 1,2-diols (8.4 mmol/L) only in slight excess to Ce^{IV} (7.4 mmol/L), but isolated hydroxyl groups in large excess. This ratio of Ce^{IV} to 1,2-diols, hereafter referred to as "grafting conditions" was found to produce optimum weight gain in our earlier studies.[1] The data in Figure 3 (asterisks) demonstrate that during the oxidation reaction, a precipitous decrease in M_n occurs within the first few minutes. Thereafter the M_n undergoes a slow, asymptotic approach to the final M_n of about 2200. Similar behavior in the presence of periodic acid indicates that chain cleavage occurs at the 1,2-diols. Isolated hydroxyl functionalities are oxidized at a slower rate but do not cause cleavage of the PVOH backbone.

These results bring into question the stoichiometry of the reaction between Ce^{IV} and 1,2-diols. The traditional view of ceric ion oxidation of PVOH[7,12-14] holds that consumption of each diol requires at least two ceric ions. As shown earlier in eq 3 and 4, one ceric ion is consumed during disproportionation of the complex and generation of a radical (eq 3), and another is consumed during oxidation of the radical in a subsequent fast reaction (eq 4). Major support for the operation of eq 4 or some similar unimacromolecular termination mechanism comes from the absence of cross-linking and gelation in ceric ion induced grafting reactions.[3] However, the data in Figure 3 shows no indication of Ce^{IV} depletion, as would be expected if each 1,2-diol consumed two ceric ions. The molecular weight (Figure 3, asterisks) was observed to fall to the limiting value of 2200, which by the periodic oxidation reaction was shown to represent cleavage of 100% of the 1,2-diols. Thus, it may be concluded in this case that each 1,2-diol consumed no more than $7.4/8.4 = 0.88$ ceric ions, but perhaps considerably less. The stoichiometry cannot be known precisely from this data alone because an unknown concentration of Ce^{IV} remained after depletion of all the 1,2-diols. Thus, in view of these results, it seems very likely that some other unimacromolecular termination mechanism is operative, in addition to or instead of eq 4.

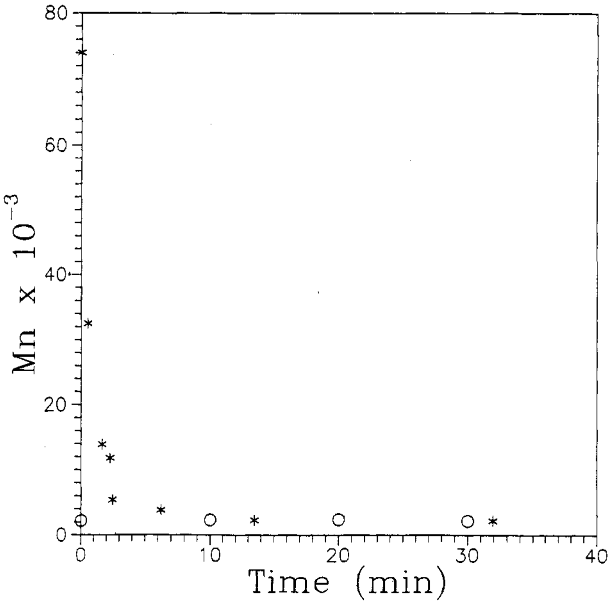
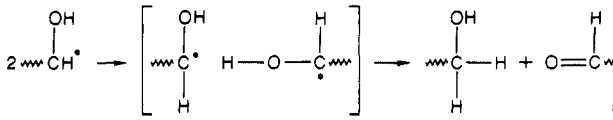


Figure 3. Exhaustive oxidative degradation of PVOH by Ce^{IV} as a function of time: (*) PVOH; (O) diol-free PVOH. [PVOH] = 19 g/L. $[Ce^{IV}]$ = 7.4 mmol/L. Temperature = 40.0 °C.

A bimacromolecular radical disproportionation mechanism is conceivable, in view of the structure of the radicals involved:



$$2\,\sim\!\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{H}^{\bullet} \longrightarrow \left[\sim\!\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}}{}^{\bullet}\quad \mathrm{H{-}O{-}}\underset{\bullet}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}\!\sim\right] \longrightarrow \sim\!\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}}\mathrm{-H} + \mathrm{O{=}}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}\!\sim \qquad (6)$$

However, the likelihood of this is not very great for two reasons. First, Hintz and Johnson[12] found that at 0 °C both hydroxyls of a 1,2-diol pair were converted to aldehyde; although it is quite relevant that they anticipated, and in fact found, that 2 mol of Ce^{IV} were reduced per mole of 1,2-diol oxidized. This is contrary to the results presented in Figure 3, but it should be noted that their reactions were run in aqueous perchloric acid solution, and more importantly, at lower temperature. Second, this mechanism does not adequately explain the results; i.e., it cannot explain the consumption of less than 1 mol of Ce^{IV}/mol of diol oxidized.

A different radical consumptive reaction that reconciles

Table II
Temperature Dependence of Ce^{IV} Oxidation of 1,2-Diols

temp, °C	Ce^{IV}/1,2-diol stoichiometry	reactn time, min	final M_n, g/mol	q, mmol/L
0.0	2.0	161	44 500	0.17
15.0	1.9	28	43 200	0.18
23.5	1.7	12	42 000	0.20
30.0	1.5	5	39 500	0.22

[PVOH] = 19 g/L
$[Ce^{IV}]$ = 0.34 mmol/L
total reaction vol = 0.115 L

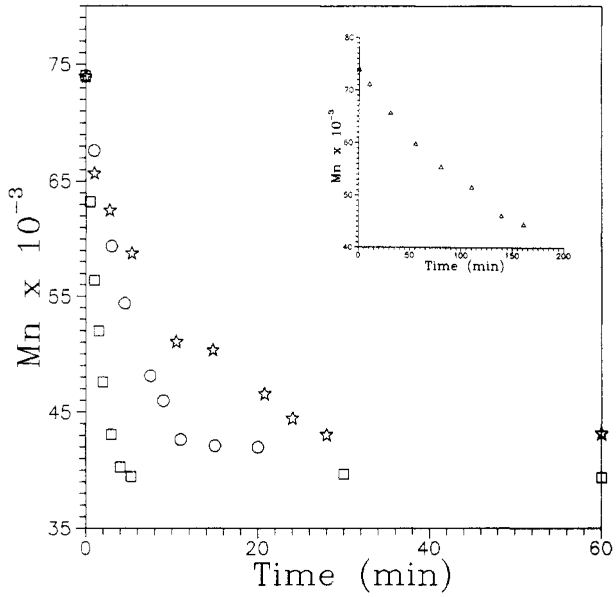
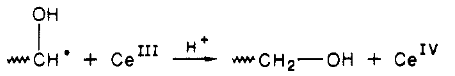


Figure 4. Partial oxidative degradation of PVOH by Ce^{IV}, under pseudo-first order conditions, as a function of time: (□) 30.0 °C; (○) 23.5 °C; (☆) 15.0 °C; (△) 0.0 °C (inset). [PVOH] = 19 g/L. $[Ce^{IV}]$ = 0.34 mmol/L.

the latter result is a reduction of the free radical intermediate by Ce^{III} as follows:



$$\sim\!\!\sim\overset{\overset{\displaystyle OH}{|}}{C}H^{\bullet} + Ce^{III} \xrightarrow{H^+} \sim\!\!\sim CH_2{-}OH + Ce^{IV} \qquad (7)$$

It is conceivable that this reaction is operative at high temperatures, e.g., 40 °C, and is responsible for the low Ce^{IV}/1,2-diol stoichiometry observed. As the temperature is lowered, this pathway is possibly suppressed, and Hintz and Johnson,[12] working at 0 °C, would indeed find a Ce^{IV}/1,2-diol stoichiometry of 2.

Further experiments were conducted to explore the temperature dependence of the Ce^{IV}/1,2-diol stoichiometric ratio. A series of oxidation reactions were run for which the temperature was varied from 0 to 30 °C, and the Ce^{IV} concentration (0.34 mmol/L) was approximately 1/25 the concentration of 1,2-diols (8.4 mmol/L). Under these conditions the concentration of 1,2-diols remains virtually constant, pseudo-first-order kinetics should be observed, and the Ce^{IV} should react exclusively with the 1,2-diols. In Figure 4 and Table II it can be seen that under these conditions there is also a significant loss in PVOH molecular weight due to backbone cleavage. Significantly, the molecular weight asymptotes at long times are greater than 2200, indicating incomplete oxidation of the 1,2-diols, and are dependent upon reaction temperature.

The cause for incomplete oxidation of 1,2-diols observed under these conditions is depletion of available Ce^{IV}. The Flory equation (eq 1) allows calculation of the millimole

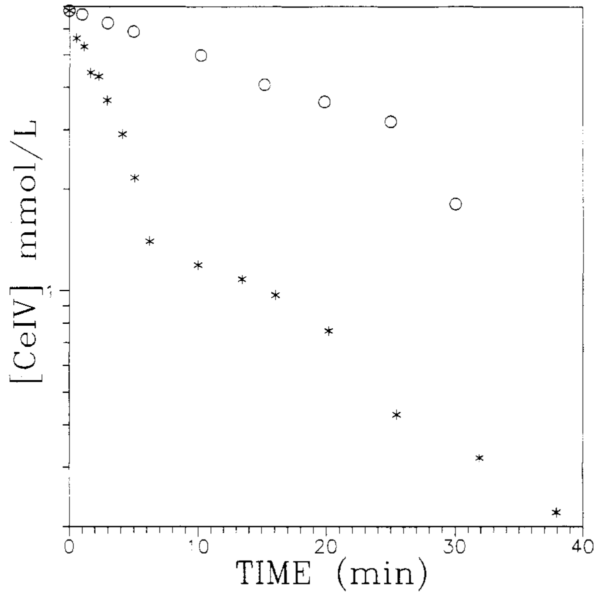


Figure 5. $[Ce^{IV}]$ as a function of time under grafting conditions: (*) PVOH; (○) diol-free PVOH. [PVOH] = 19 g/L. $[Ce^{IV}]$ = 6.8 mmol/L. Temperature = 40.0 °C.

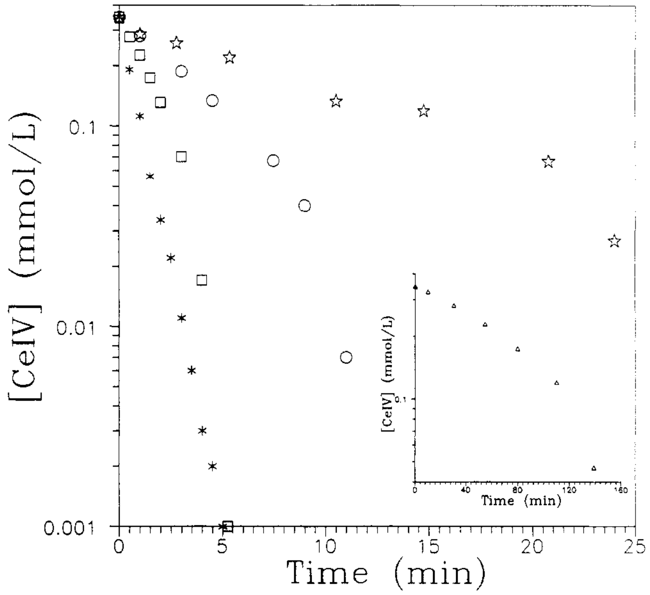


Figure 6. $[Ce^{IV}]$ as a function of time under pseudo-first-order conditions: (*) 40.0 °C; (□) 30.0 °C; (○) 23.5 °C; (☆) 15.0 °C; (△) 0.0 °C (inset). [PVOH] = 19 gL. $[Ce^{IV}]$ = 0.34 mmol/L.

chain cleavages per liter, q, listed in Table II, which occurred in order to reach these particular molecular weights. For example, at 23.5 °C, q = 0.20 mmol/L (see Appendix A). Initially, $[Ce^{IV}]$ = 0.34 mmol/L, indicating that at 23.5 °C each 1,2-diol consumed 1.7 ceric ions. The Ce^{IV}/1,2-diol stoichiometry observed for each temperature is listed in Table II. Clearly, the consumption of Ce^{IV} per 1,2-diol increases as the reaction temperature decreases. Note that as the temperature is lowered to 0 °C, the stoichiometry approaches 2.0, which is in perfect agreement with the findings of Hintz and Johnson.[12]

The results in Table II suggest that the widely held view of Ce^{IV} oxidation of 1,2-diols, i.e., the fast oxidation of formed free radicals by additional ceric ion (eq 4), must be modified to include some other radical-consumptive mechanism which becomes increasingly important at elevated temperatures. In view of the results at 40 °C under grafting conditions, it is suggested that a fast reduction of radicals by Ce^{III} occurs (eq 7). This would regenerate

Table III
Pseudo-First-Order Rate Constants for Reaction of Ce^{IV} with Excess 1,2-Diols

temp, °C	k, min^{-1}	temp, °C	k, min^{-1}
0.0	0.013	30.0	0.48
15.0	0.085	40.0	0.89
23.5	0.20		

Ce^{IV} and yield an overall requirement of less than one ceric ion per 1,2-diol. This hypothesis is presently under investigation.

The kinetics of oxidation of PVOH by Ce^{IV} was also followed by monitoring the disappearance of ceric ion by titration.[13] The results obtained under grafting conditions and under pseudo-first-order conditions are shown in Figures 5 and 6, respectively. Under grafting conditions, $[Ce^{IV}] \cong [1,2\text{-diol}]$, but isolated hydroxyl groups are in large excess. This should reduce the reaction with isolated hydroxyls to a pseudo-first-order reaction with respect to ceric ion.

The curve for PVOH in Figure 5 (asterisks) can be divided into two processes. At first, there is a rapid decrease in Ce^{IV} concentration due to reaction with 1,2-diols, followed by a slower, first-order reaction with isolated hydroxyls. The break in the curve occurs at $[Ce^{IV}] = 1.4$ mmol/L. If it is assumed that this point represents depletion of 1,2-diols, the Ce^{IV}/1,2-diol stoichiometry was ~0.65. The pseudo-first-order rate constant for reaction of Ce^{IV} with isolated hydroxyls was measured to be 0.040 min^{-1}. The initial slope of the rapid decrease portion of the curve yielded a value of 0.21 min^{-1}; however, this reaction is not first-order since it exhibits an accelerating downward curvature.

When the oxidation reaction was run under pseudo-first-order conditions, as shown in Figure 6, the downward curvature was not observed at 40 °C, but it was evident at lower temperatures toward the end of the reaction. The precise cause of this rate acceleration is unknown at this time. However, the plots are quite linear during the early stages of the reaction, yielding pseudo-first-order rate constants which are listed in Table III. These were observed to follow an Arrhenius temperature dependency, as depicted in Figure 7. The activation energy and preexponential factor were found to be 18.3 kcal/mol and 6.1×10^{12} min^{-1}, respectively. The value of $k = 0.20$ min^{-1} obtained unknown 23.5 °C is very reasonable since Mino et al.[7] obtained a value of 0.11 min^{-1} at 20 °C. As a further note, if one compares the initial slopes of the 40 °C reactions under pseudo-first-order conditions (0.89 min^{-1}) and grafting conditions (0.21 min^{-1}), it is seen that the rate of depletion of Ce^{IV} is much greater under pseudo-first-order conditions, i.e., when $[Ce^{IV}]/[1,2\text{-diols}] \ll 1.0$. This suggests that under grafting conditions, complexation of Ce^{IV} occurs with both 1,2-diols and isolated hydroxyls, and this effectively limits the Ce^{IV} available for reaction with 1,2-diols. As pointed out earlier, reaction with both 1,2-diols and isolated hydroxyls should lead to a mixture of block and graft copolymers. However, as the $[Ce^{IV}]/[1,2\text{-diol}]$ ratio is lowered, oxidation tends to occur more and more exclusively with 1,2-diols, which produces block rather than graft copolymers. Thus, if one desires an exclusively block copolymer product, the $[Ce^{IV}]$ should be kept very low, for example, by a starve-feed mode of addition of Ce^{IV} to the reaction mixture.

Oxidation of Diol-Free PVOH. For comparison, diol-free PVOH ($M_n = 2200$) was subjected to the same reactions as was virgin PVOH. Diol-free PVOH was produced by periodic oxidation of PVOH,[7] and to ensure the absence of terminal aldehyde groups, the polymer was subsequently treated with sodium borohydride.

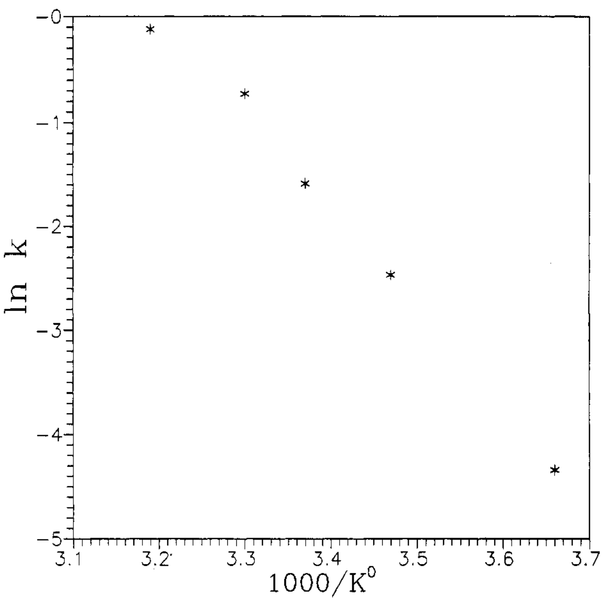


Figure 7. Arrhenius plot for reaction of Ce^{IV} with PVOH 1,2-diols under pseudo-first-order conditions.

As shown in Figure 3 (circles) the molecular weight of diol-free PVOH was unaffected during oxidation by Ce^{IV}. This reaffirms that oxidation of isolated hydroxyls does not lead to chain cleavage and therefore would initiate a true graft copolymer chain.

The pseudo-first-order rate constant for oxidation of diol-free PVOH with Ce^{IV} was determined to be 0.040 min^{-1} from the slope of the diol-free PVOH curve in Figure 5 (circles). This value is in agreement with the rate constant for the oxidation of the commercial PVOH after all the 1,2-diols had been oxidized (Figure 5, PVOH curve for time > 10 min). Also, this confirms that the second, slower rate is due to the isolated hydroxyls on the PVOH backbone, and it demonstrates that the majority of 1,2-diols are oxidized within the first 10–15 min of the reaction. This is in agreement with previous work.[5]

Conclusion

Dramatic differences in the PVOH/PVDC copolymer products were observed as the $[Ce^{IV}]/[1,2\text{-diol}]$ concentration ratio was varied over a large range. These differences may be explained in terms of the competition for Ce^{IV} between 1,2-diols and isolated hydroxyls. The final M_n of the PVOH segments is dependent on the mole percent 1,2-diol content and the initial concentration of Ce^{IV}. Under conditions of high $[Ce^{IV}]$, the product is envisioned as a small PVOH segment with numerous block and grafted segments. This causes the product properties to be dominated by the PVDC segments. In systems where $[Ce^{IV}]$ is lower, the PVOH segment is believed to remain larger, and the product is predominantly a block copolymer. Because this product retains a high weight fraction of PVOH, it displays unique properties that are different from either homopolymer.

The oxidation of PVOH occurs most readily at the 1,2-diol linkage of the PVOH backbone. The reaction of Ce^{IV} with 1,2-diols was studied by observing the decrease in M_n of PVOH. Exhaustive oxidation by either Ce^{IV} or periodic acid led to PVOH fragments of $M_n = 2200$. This result allowed calculation of the mole percent 1,2-diol content, which in this case was 1.9 mol %. It also showed that at relatively high temperatures, i.e., 40 °C, the Ce^{IV}/1,2-diol stoichiometric ratio was actually less than 1.0.

This result lead to further reaction studies in which Ce^{IV} was chosen to be the limiting reagent. Under these conditions of low ceric ion concentration the stoichiometry of Ce^{IV} to 1,2-diols was observed to increase from 1.5 at 30 °C to 2.0 at 0 °C. The value of 2.0 at 0 °C is in agreement with prior work of others.[12] These results suggest that the traditional view of Ce^{IV} oxidation of 1,2-diols, i.e., the fast oxidation of previously formed free radicals by additional ceric ion (eq 4), must be modified to include some other radical-consumptive mechanism operative at higher temperatures. It is suggested that this might involve a fast reduction of free radicals by Ce^{III} (eq 7), which is formed in the initial step of the reaction.

From Ce^{IV} titration data under "grafting conditions", a majority of the Ce^{IV} was shown to be depleted early in the reaction due to oxidation of 1,2-diols. A second rate of oxidation due to isolated hydroxyls was seen thereafter. The pseudo-first-order rate constants for this second rate and that of diol-free PVOH are the same, i.e., 0.040 min^{-1} at 40 °C. Under conditions of low $[Ce^{IV}]$, titration data yielded a pseudo-first-order rate constant with respect to ceric ion with a temperature dependence defined by $k = 6.1 \times 10^{12} \exp(-18.3\ \mathrm{kcal}/RT)\ \mathrm{min}^{-1}$. The value of $k = 0.20\ \mathrm{min}^{-1}$ at 23.5 °C is in reasonable agreement with Mino et al.,[7] who found a value of 0.11 min^{-1} at 20 °C. An accelerating downward curvature was observed in most of the first-order plots toward the end of the reaction; this phenomenon is poorly understood at this time.

These results indicate that the redox reaction between Ce^{IV} and PVOH is indeed a complex one. The reaction stoichiometry, and therefore the mechanism, has been shown to change dramatically over a relatively narrow temperature range. However, the reaction conditions can be controlled to optimize the physical properties of the resulting PVOH/PVDC copolymer, and if proper conditions are employed, it is conceivable that predominantly block copolymers can be produced.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Appendix A

The millimole chain cleavages per liter, q, is given by the fraction of chain repeat units cleaved, Δ

$$\Delta = M_0(1/M_n - 1/M_{n0})$$

where

$$M_0 = 44\ \mathrm{g/mol}$$

$$M_{n0} = 74\,000\ \mathrm{g/mol}$$

and at 23.5 °C

$$M_n = 42\,000\ \mathrm{g/mol}$$

multiplied by the molar concentration of PVOH repeat units in the oxidation reaction:

$$q = \Delta([\mathrm{PVOH}]/M_0) = 0.20\ \mathrm{mmol/L}$$

Registry No. PVOH, 9002-89-5; CAN, 10139-51-2; (VOH)(VDC) (block copolymer), 117556-92-0; (VOH)(VDC) (graft copolymer), 108917-82-4; VDC, 75-35-4.

References and Notes

(1) Storey, R. F.; Sudhakar, D.; Goff, L. J. *J. Makromol. Sci., Chem.* **1987**, *A24*(9), 1051–1064.
(2) McDowall, D. J.; Gupta, B. S.; Stannett, V. T. *Prog. Polym. Sci.* **1984**, *10*, 1–50.
(3) Mino, G.; Kaizerman, S. *J. Polym. Sci.* **1958**, *31*, 242.
(4) Iwakura, Y.; Imai, Y. *Makromol. Chem.* **1966**, *98*, 1–6.
(5) Ogiwara, Y.; Uchiyama, M. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 1479–1488.
(6) Narita, H.; Okamoto, S.; Machida, S. *Makromol. Chem.* **1969**, *125*, 15–23.
(7) Mino, G.; Kaizerman, S.; Rasmussen, E. *J. Polym. Sci.* **1959**, *39*, 523–529.
(8) Flory, P. J.; Leutner, F. S. *J. Polym Sci.* **1948**, *3*(6), 880–890.
(9) Molyneaus, P. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC: Boca Raton, FL, 1984; Vol. I.
(10) Finch, C. A. *Polyvinyl Alcohol*; Wiley: New York, 1973.
(11) Mino, G.; Kaizerman, S.; Rasmussen, E. *J. Am. Chem Soc.* **1959**, *81*, 1494.
(12) Hintz, H. L.; Johnson, D. C. *J. Org. Chem.* **1967**, *32*, 556–564.
(13) Duke, F. R.; Forist, A. A. *J. Am. Chem. Soc.* **1949**, *71*, 2790–2792.
(14) Duke, F. R.; Bremer, R. F. *J. Am. Chem. Soc.* **1951**, *73*, 5179–5181.
(15) Duke, F. R.; Smith, G. R. *Ind. Eng. Chem., Anal. Ed.* **1940**, *12*, 201.
(16) Young, L. B.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1969**, *91*(18), 5060–5067.
(17) Mino, G.; Kaizerman, S.; Rasmussen, E. *J. Polym. Sci.* **1959**, *38*, 393.
(18) Saha, S. K.; Choudhury, A. K. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 1505.