JOURNAL OF POLYMER SCIENCE VOL. XXXIX, PAGES 335–345 (1959)

Stereoregulated Polymerization in the Free Propagating Species. II. Effect of Monomer Structure on the Polymerization of Vinyl Esters*

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INTRODUCTION

In the first paper of this series[1] the theory of stereoregulation at the free end of a growing polymer chain was presented. One of the predictions from that treatment was that the syndiotactic configuration in polymers produced by a free radical mechanism could be favored over the competing isotactic configuration by steric and electrostatic factors in the monomer structure. The present publication is concerned with the experimental verification of this hypothesis for the specific case of vinyl esters. The vinyl ester series was selected for the study because changes in size and polarity in the monomer can be readily achieved by replacing the hydrogen atoms of the acetoxy substituent with halogen atoms. Furthermore, the esters contain the strong carbonyl dipole which should favor the preferred placement. The specific monomers that were used in the investigation can be represented by the general formula: $CH_2{=}CHOOCCH_{3-n}X_n$, where $X = Cl$ or F and $n = 0, 1, 2,$ or 3.

EXPERIMENTAL

Preparation of Monomers

The monomers to be polymerized were purified by fractionation through a spinning band column. The vinyl acetate that was fractionated was the commercial grade. The unavailable vinyl haloacetates were prepared by standard liquid phase vinylation of the corresponding acid (chloro[2] and fluoro[3]). In the synthesis of vinyl trichloroacetate the acid was mixed with an equimolar weight of benzene to liquify the reaction mixture at the vinylation temperature. Identifying physical properties of the four haloesters are listed in Table I. Elemental analysis of the vinyl monochloroacetate gave values of 40.0% C (theor. 39.9%), 4.19% H (theor. 4.18), and 29.3% Cl (theor. 29.4%).

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* Presented at the 133rd Meeting of the American Chemical Society, Division of Polymer Chemistry, San Francisco, April 1958.

TABLE I
Physical Properties of $CH_2{=}CHOOCR$

R	B.p. (obs.), °C.	B.p. (lit.), °C.	n_D (obs.)	n_D (lit.)	Reference
CH_2Cl	47^{20}	59^{50}	1.4422^{25}	1.4438^{21}	2
$CHCl_2$	46^{28}	—	1.4579^{21}	—	—
CCl_3	46^{13}	68^{42}	1.4662^{21}	1.4670^{20}	4
CF_3	40^{750}	40^{760}	1.3140^{25}	1.3106^{25}	3

Polymerization

All polymerization was done in sealed glass tubes from which oxygen had previously been removed either by evacuation or by flushing with high purity nitrogen. The actual polymerization conditions used to achieve substantially complete conversion are presented in Table II. The chloroacetate polymers become increasingly unstable as the number of chlorine substituents increases. Polyvinyl trichloroacetate darkens badly on standing for only a few days. The copolymerization of vinyl monochloroacetate and vinyl acetate to determine reactivity ratios was done with benzoyl peroxide (0.10 g./mole of monomers) as initiator at 60°C. The low conversion copolymers were purified by three precipitations from distilled tetrahydrofuran solution with distilled *n*-heptane.

TABLE II
Conditions for Polymerizing $CH_2{=}CHOOCR$

R	Peroxide	Peroxide concn., %	Temp., °C.	Time, hr.
CH_3	Lauroyl	0.10	45	120
CH_2Cl	"	0.10	45	120
$CHCl_2$	"	0.10	45	72
CCl_3	Benzoyl	0.20	60	72
CF_3	"	0.20	60	24

Preparation of Polyvinyl Alcohol

The conversion of the polyvinyl haloacetates to the alcohol was done under basic and relatively mild conditions to minimize side reactions. Methanolysis was used generally to form the alcohol. However, the highly oriented polyvinyl alcohol was prepared by ammonolysis. The methanolysis was effected in a tetrahydrofuran–methanol mixture kept basic with sodium methylate. The reaction was initially done at room temperature and finished at reflux temperature. Alcoholysis was essentially complete on the basis of saponification and halogen analysis data. Ammonolysis of the polyvinyl trifluoroacetate was done at room temperature. A thin film, previously stretched to 15 times its original length at 100°C., was exposed to an atmosphere of anhydrous ammonia for several days. The stretched alcohol film was purified by extraction with cold methanol.

RESULTS

Polyvinyl Esters

The effect of changing substituents in the R group of $CH_2{=}CHOOCR$ results in a significant change in the unoriented x-ray patterns, which are reproduced in Figure 1. In the polymer of the unsubstituted vinyl acetate, the halos are diffuse. The chloroacetate polymers give sharper halos which, although still of amorphous character, do suggest some improvement in the packing of the chains and hence the order of the substituents along the backbone. In polyvinyl trifluoroacetate, a truly crystalline line appears as an inner ring in addition to an amorphous halo. The Bragg *d* spacings for the five polyvinyl esters are tabulated in Table III.

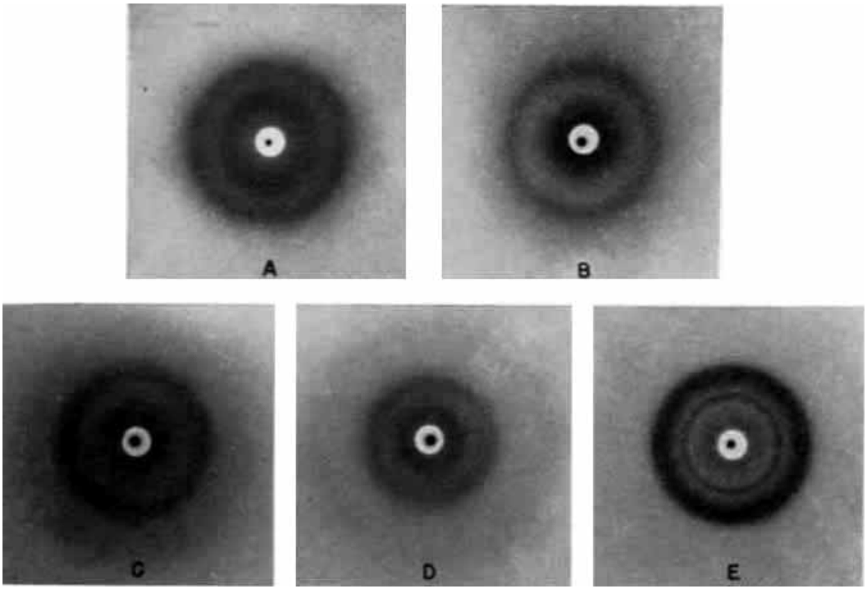

Fig. 1. X-ray patterns of unstretched polyvinyl esters: (A) acetate; (B) monochloroacetate; (C) dichloroacetate; (D) trichloroacetate; (E) trifluoroacetate. Ni-filtered CuKα radiation.

TABLE III

d Spacings for Polymers of $CH_2{=}CHOOCR$

R	d_1, A.	d_2, A.	d_3, A.
CH_3	6.20 (s)	4.00 (s)	—
CH_2Cl	4.15 (s)	—	—
$CHCl_2$	4.45 (s)	2.90 (m)	—
CCl_3	4.95 (s)	2.85 (m)	2.05 (w)
CF_3	6.25 (s)	4.15 (s)	—

Of the polyvinyl esters only the trifluoroacetate shows a preferred orientation on stretching. The patterns of the other stretched polymers are very similar to the amorphous patterns of the corresponding unstretched specimens. The lack of appearance of true crystallinity by stretching makes less likely the possibility that these polymers are crystallizable and can be crystallized by applying special treatment. The trifluoroacetate is very similar to that reported previously.[3] The equatorial arcs are sharper than the diffuse meridional arcs. Respective widths at half-maximum intensity are 1.7 and 4.3°. Hence, the oriented crystallites are small and resemble wafers with the small dimension along the fiber axis. In spite of the small mean size of the crystallites, the degree of crystallinity is estimated visually to be about 80%. The repeat distance along the fiber axis is 4.8 ± 0.1 A. Unequivocal determination of unit cell dimensions was not possible because of lack of sufficient number of reflections in the pattern. However the unit cell is probably monoclinic with β larger than 100°.

Polyvinyl Alcohol

Additional evidence for the same order of regularity in the polyvinyl esters can be obtained by an examination of the solubility behavior of the derived polyvinyl alcohols. Conversion of a simple ester to an alcohol under basic conditions proceeds with acyl-oxygen fission and not alkyl-oxygen fission.[5] Hence the polyvinyl alcohol should possess the same steric configuration along the chain as the parent ester polymer. The water resistance of the various alcohol polymers is presented in Table IV. The swelling index decreases as the parent polymer changes from unsubstituted acetate to a chloroacetate to trifluoroacetate, and thereby indicates increasing regularity in the same order. The results also suggest that the polymers of the vinyl polychloroacetates are more regular than the monochloroacetate polymer. Significantly, the polyvinyl alcohols from the haloacetates are all insoluble in hot water, in contrast to the complete solubility of the alcohol from the acetate. The insolubility of the present polyvinyl alcohol derived from the trifluoroacetate substantiates the earlier finding of Haas et al.[3]

TABLE IV
Water Resistance of Polyvinyl Alcohols from Polymers of $CH_2{=}CHOOCR$

R	η_{sp}/c, dl./g.[a]	Swelling index[b]
CH_3	4.9	∞
CH_2Cl	1.5	21
$CHCl_2$	0.9	5
CCl_3	0.9	6
CF_3	1.2	4

[a] Parent ester polymer at a concentration of 0.1 g./100 ml. of cyclohexanone and at 25°C.

[b] Weight of water imbibed at 70°C. per unit weight of polymer.

The possibility that other structural variations are responsible for the above differences in solubility is considered to be highly unlikely. The molecular weight parameter does not seem to be the causative factor, because the change in swelling index with the viscosity number of the parent polyvinyl ester (and presumably the derived alcohol) is generally the reverse of the trend expected from a molecular weight consideration. Insolubility because of chemical crosslinking is not attractive, since the polyvinyl alcohol from the monochloroacetate dissolves in a hot concentrated thiocyanate solution. Secondly, the incorporation of small quantities of vinyl acetate (VAc) into the parent polymer destroys the insolubility of the derived alcohol in boiling water (Table V). The presence of small quantities of acetate would not be expected to change significantly chemical crosslinking. However, the same small quantities of acetate could conceivably interrupt regularity in the parent polymer and hence in the derived alcohol. It should be emphasized that the loss of insolubility is not due to chemical irregularity, because the alcohol is, of course, a chemical homopolymer even though derived from a copolymer. The extreme sensitivity of solution properties to structure in this particular case is demonstrated by the fact that addition of only 2 mole-% of vinyl acetate to the monochloroacetate yields a soluble polyvinyl alcohol. With the trifluoroacetate, larger concentrations of interfering acetate are required. Once again, the greater regularity in the trifluoroacetate polymer than in the chloroacetate is indicated.

TABLE V

Solubility of Polyvinyl Alcohols from Copolymers of CH_2=CHOOCR and VAc

R	VAc, mole-%	Solubility[a]
CH_2Cl	0.8	insol.
CH_2Cl	1.2	insol.
CH_2Cl	2.4	sol.
CF_3	4.7	insol.
CF_3	7.9	insol.
CF_3	15.0	sol.

[a] In water at 100°C.

The x-ray investigation of the polyvinyl alcohol derived from the trifluoroacetate did not yield conclusive results on chain structure. From a pattern similar to that obtained previously[3] the chain repeat distance was found to be 2.5 A. and not 5 A. as in the parent polymer. This difference is believed to be due to the similarity in the size of the hydrogen and hydroxyl substituents rather than to racemization during alcohol formation. The two substituents on the pseudoasymmetric carbon atom are sufficiently similar in size so that they are interchangeable in the positions of the crystal lattice.[6] The actual difference in size does not prohibit interchange, because the crystal lattice of polyvinyl alcohol is relatively loose with large hydrogen bond distances. As a result, polyvinyl alcohol with an atactic, isotactic, or syndiotactic structure could have a repeat distance of 2.5 A.

For the syndiotactic configuration, the second chain in the unit cell is postulated to slip one-half of the repeat distance randomly in either direction along the fiber axis.[7] A detailed analysis of the best possible fiber pattern is required to establish directly the structure of the polyvinyl alcohol from the trifluoroacetate.

Vinyl Chloroacetate Copolymerization

The reactivity ratios r_1 and r_2 for vinyl chloroacetate (VClAc)—vinyl acetate were determined from the equation:[8]

$$(f - 1)/F = r_1 - (f/F^2)r_2$$

where $f = m_1/m_2$, with m referring to copolymer composition, and $F = M_1/M_2$, with M referring to monomer composition. The copolymer compositions, based on triplicate chlorine determinations, give the curve of Figure 2. The least squares line through the corresponding values of $(f - 1)/F$ and f/F^2 in Figure 3 yields an r_1 of 1.20 and r_2 of 0.73 with chloroacetate as M_1 and acetate as M_2. The proximity of both ratios to unity implies random copolymerization as would be expected from two monomers of such similar general structure.

The above reactivity ratios were used to calculate the monomer reactivity factors for vinyl monochloroacetate. The Q and e values for the acetate, monochloroacetate, and trifluoroacetate are compared in Table VI. The value of e, associated with the polarity of the double bond, becomes increasingly positive in the order:

acetate < monochloroacetate < trifluoroacetate

The Q value, usually related to resonance, is relatively unchanged in the three monomers.

TABLE VI
Reactivity Factors for CH_2=CHOOCR

R	e	Q
CH_3[a]	−0.5	0.024
CH_2Cl	−0.1	0.027
CF_3[b]	0.8	0.022

[a] Reference 9.
[b] Reference 3.

DISCUSSION

Electrostatic and Steric Effects

The foregoing results on polymer structure show that the nature of the substituent group in the monomer plays an important role in determining the regularity of polyvinyl esters prepared with the use of free radical

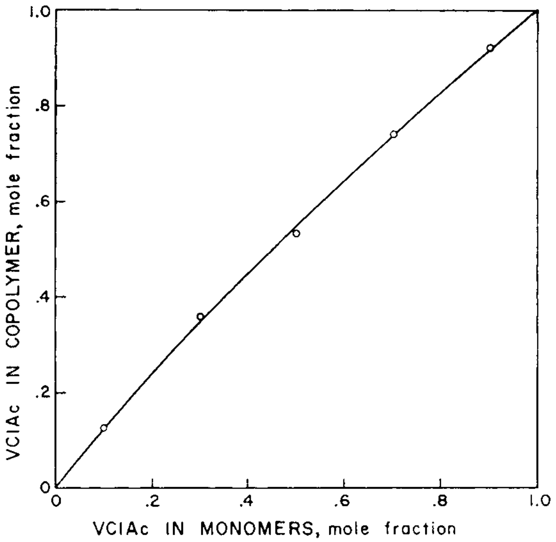

Fig. 2. Copolymer composition curve for VClAc–VAc.

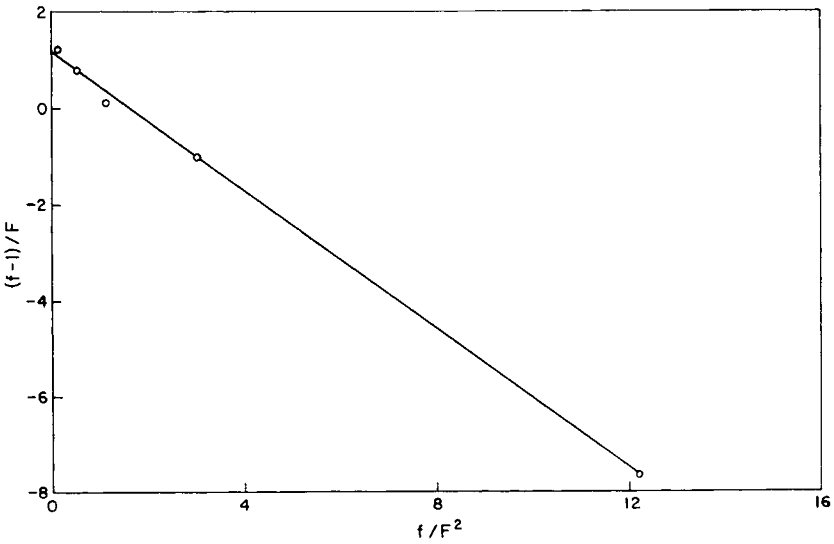

Fig. 3. $(f - 1)/F$ vs. f/F^2 for VClAc–VAc Copolymerization.

initiators. The degree of regularity in these polymers appears to increase in the order:

acetate < monochloroacetate < polychloroacetates < trifluoroacetate

The influence of the substituent group in this series of monomers is limited, however, because the regular sequences are relatively short, even in the most regular trifluoroacetate. The lack of detail in the x-ray patterns and diffuseness of the meridional arcs indicate a regular sequence length of only a few units. The short sequence length and the high degree of crystallinity suggest that the polyvinyl trifluoroacetate consists of numerous sequences of one configuration interrupted at short intervals by the other configuration.

With respect to the basic factors of the substituent group, the electrostatic component seems to be more important than the steric factor in the polyvinyl ester series. The above series of increasing regularity parallels increasing polarity in the substituent group, but not always increasing size. The same order in increasing polarity can be seen in the *e* values for the monomers (Table VI) and also in the strengths of the corresponding acids (Table VII). As the methyl substituents become successively more electronegative, induced electronegativity at the ester oxygen is also increased. Hence there is an increasing tendency for the polarizable electrons to be withdrawn from the double bond and give the observed change in *e* to more positive values. In the case of the acid the electrons are pulled from the hydrogen atom, which permits easier ionization. The series does not correlate with increasing substituent size because the trifluoromethyl group is, of course, smaller than the trichloromethyl group. The relative unimportance of the steric factor is not surprising, since the change in size is made at the end of the acyl group and its influence can be diminished by rotation around the bonds of the flexible ether oxygen linkage. The polar effect, on the other hand, has been shown above to be significant beyond the terminal acyl group.

TABLE VII
Dissociation Constants of RCOOH[a]

R	K_A
CH_3	1.75×10^{-5}
CH_2Cl	1.40×10^{-3}
$CHCl_2$	5.00×10^{-2}
CCl_3	1.30×10^{-1}
CF_3	5.00×10^{-1}

[a] Reference 10.

The importance of the polarity of the substituent is also supported by the results on other stereoregulated radical polymerizations. Strongly polar substituents are present in the only other two examples reported to date: polymers of vinyl chloride[11] and methyl methacrylate.[12,13] Regularity in polymethyl methacrylate prepared with a radical initiator may be aided by the smaller electronegativity of the methyl group as compared to the hydrogen substituent in a vinyl polymer. Furthermore, it may be significant that stereoregular polymers from nonpolar hydrocarbons by a free radical mechanism have not yet been reported.

Configuration of Regular Sequences

The repeat distance along the polyvinyl trifluoroacetate chain indicates that the regular sequences have a syndiotactic configuration. While the experimental value of 4.8 A. is not in exact agreement with the theoretical value of 5.0 A. for an extended syndiotactic zigzag,[14] the measured value is markedly different from the values for the simplest arrangements of the isotactic configuration. The theoretical repeat distance for the 1_1 zigzag is 2.5 A., and for the 3_1 helix, 6.2 A.[14] The observed lowering of the repeat distance from the theoretical value could arise from a twisting of the chain carbon atoms by the strong electrostatic repulsion in the trifluoroacetoxy substituents. In other words, the zigzag is not fully extended. The same shortening has been noted for the symmetrical polymer of vinylidene chloride, which is also believed to have two units per repeat interval.[15] Further proof of the structure of the trifluoroacetate must await a more detailed fiber pattern.

The preferred propagation for free radical stereoregulated polymerization appears to be syndiotactic rather than isotactic, in agreement with the theoretical prediction for the representative vinyl chloride polymerization.[1] In all reported regular polymers prepared by a free radical mechanism (polyvinyl trifluoroacetate, polyvinyl chloride,[11] and polymethyl methacrylate[12,13,16]), the regular structure is thought to be syndiotactic. It is conceivable that syndiotactic propagation is preferred for free radical polymerization in general, and polymers prepared by a radical mechanism are more regular than has previously been suspected.

The assistance of others in the experimental investigation is gratefully acknowledged. Members of the Diamond Alkali Research Department who participated in the work comprise Mr. J. M. Strong (syntheses), Mr. I. E. Smiley (x-ray analyses), and Mr. H. N. Benedict and his group (wet analyses). Part of the x-ray investigations were done by Mr. G. G. Summer of Mellon Institute and, initially, by Dr. G. L. Clark of the University of Illinois.

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Synopsis

The first paper of the series contained the theoretical prediction that syndiotactic propagation could be favored over isotactic propagation in free radical polymerization by the nature of the monomer substituent group. To check this hypothesis the steric structure of polymers of vinyl acetate and certain haloacetates was investigated. X-ray examination of the polyvinyl esters and the solubility of derived alcohol polymers indicate that the degree of regularity increases in the order: acetate < monochloroacetate < polychloroacetates < trifluoroacetate. The influence of the substituent group is limited in the polyvinyl esters because only the trifluoroacetate shows true crystallinity, and, even in this polymer, the average length of the regular sequences appears to be small. The above order of regularity suggests that the electrostatic factor is more important than the steric factor in the stereoregulated polymerization of vinyl esters. The regular sequences of the trifluoroacetate are indicated to have a syndiotactic configuration from the chain repeat distance. The polymerization of the ester is believed to involve predominantly syndiotactic propagation, with relatively frequent interruptions of isotactic propagation. The generalizations agree with results reported for other stereoregular radical polymerizations. Conceivably, syndiotactic propagation may be preferred for free radical polymerization in general, and polymers produced under radical conditions may be more regular than has been realized.

Résumé

Le premier article de cette série contenait la prédiction théorique que la propagation syndiotactique serait favorisée par rapport à la propagation isotactique dans la polymérisation radicalaire suivant la nature du groupe substituant du monomère. Pour prouver cette hypothèse, on a étudié la structure stérique des polymères d'acétate de vinyle et certains haloacétates. L'examen aux rayons-x des polyesters de vinyle et la solubilité des dérivés alcooliques des polymères indiquent que le degré de régularité augmente dans l'ordre: acétate < monochloroacétate < polychloroacétates < trifluoroacétate. L'influence du groupe substituant dans les polyesters de vinyle est limitée parce que seulement le trifluoroacétate montre une cristallinité réelle et même dans ce polymère la longueur moyenne des séquences régulières semble être très petite. L'ordre de régularité indiqué plus haut suggère que le facteur électrostatique est plus important que le facteur stérique dans la polymérisation stéréorégularisée des esters de vinyle. On montre que les séquences régulières du trifluoroacétate sont d'une configuration syndiotactique et cela à partir de la distance séparant les séquences. On croit que la polymérisation de l'ester implique une propagation syndiotactique prédominante avec des interruptions relativement fréquentes de propagation isotactique. Ces généralisations sont en accord avec les résultats obtenus à partir des polymérisations stéréorögularisées radicalaires. En général on préfère la propagation syndiotactique pour la polymérisation radicalaire et des polymères produits sous des conditions radicalaires peuvent probablement être plus réguliers que ceux qui ont été réalisés.

Zusammenfassung

In der ersten Mitteilung dieser Reihe wurde die theoretische Voraussage ausgesprochen, dass bei einer radikalischen Polymerisation das syndiotaktische Wachstum gegenüber dem isotaktischen Wachstum durch die Natur der substituierenden Gruppe im Monomeren begünstigt werden könnte. Zur Uberprüfung dieser Hypothese wurde die sterische Struktur von Polymeren des Vinylacetats und gewisser Halocetate untersucht. Röntgenuntersuchungen an den Polyvinylestern und die Löslichkeit der davon abgeleiteten polymeren Alkohole sprechen dafür, dass der Grad der Regelmässigkeit in der Reihenfolge: Acetat < Monochloracetat < Polychloracetate < Trifluoracetat zunimmt. Der Einfluss der substituierenden Gruppe ist bei den Polyvinylestern ein beschränkter, da nur die Trifluoracetate wahre Kristallinität zeigen, und sogar bei diesem Polymeren scheint die mittlere Länge der regelmässigen Sequenzen klein zu sein. Die oben angegebene Reihenfolge bezüglich der Regelmässigkeit weist darauf hin, dass der elektrostatische Faktor bei der sterisch geregelten Polymerisation von Vinylestern wichtiger ist als der sterische Faktor. Die regelmässigen Sequenzen des Trifluoracetates haben, nach den periodischen Kettenabständen zu schliessen, eine syndiotaktische Konfiguration. Es wird angenommen, dass die Polymerisation der Ester vorwiegend mit syndiotaktischem Wachstum, bei verhältnismässig häufiger Unterbrechung durch isotaktisches Wachstum, verläuft. Die allgemeinen Folgerungen stimmen mit den Resultaten an anderen sterisch geregelten Radikalpolymerisationen überein. Es ist denkbar, dass syndiotaktisches Wachstum allgemein bei radikalischer Polymerisation bevorzugt sein kann und dass Polymere, die unter den Bedingungen der radikalischen Polymerisation gebildet wurden, regelmässiger gebaut sind als bisher angenommen wurde.

Received January 22, 1959