Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Acid-Catalyzed Methanolysis of Vinyl Acetate Polymers and Copolymers. I. Polyvinyl Acetate

C. Pichot[a]; J. Guillot[a]; A. Guyot[a]
[a] Laboratoire de Cinetique Chimique Macromoleculaire Universite "Claude Bernard", Villeurbanne, France

To cite this Article Pichot, C. , Guillot, J. and Guyot, A.(1974) 'Acid-Catalyzed Methanolysis of Vinyl Acetate Polymers and Copolymers. I. Polyvinyl Acetate', Journal of Macromolecular Science, Part A, 8: 6, 1073 — 1086

To link to this Article: DOI: 10.1080/00222337408066421

URL: http://dx.doi.org/10.1080/00222337408066421

J. MACROMOL. SCI.—CHEM., A8(6), pp. 1073-1086 (1974)

Acid-Catalyzed Methanolysis of Vinyl Acetate Polymers and Copolymers. I. Polyvinyl Acetate

C. PICHOT, J. GUILLOT, and A. GUYOT

Laboratoire de Cinétique Chimique Macromoléculaire
Université "Claude Bernard"
Villeurbanne, France

ABSTRACT

Acid (HCl) catalyzed methanolysis of polyvinyl acetate and of model compounds was carried out in solvent mixtures with various amounts of methanol and tetrahydrofuran. The initial rate was first order vs methanol concentration. The acceleration was mainly dependent on the extension of the chain and was enhanced by a tighter coiling of the macromolecule; it is suggested that coiling favors the trapping of the catalyst ions.

INTRODUCTION

The purpose of this series of papers is to show the relationship between the sequence distribution and the chemical reactivity of a copolymer. Alcoholysis of vinyl acetate copolymers, including chlorinated copolymers, was employed and, because of the product studied, it was decided to use acid catalysis in the presence of tetrahydrofuran in order to obtain a homogeneous reaction.

Only a few studies have been devoted to the acid-catalyzed alcoholysis of polyvinyl acetate compared to the well-known base-catalyzed hydrolysis. Minsk, Priest, and Kenyon [1] have shown the similarity of the behavior of the two processes (approximately first order vs catalyst concentration, autoacceleration) although the mechanisms briefly summarized in Fig. 1 are rather different [2]. More recent studies have shown that the proton concentration in an acid medium is strongly dependent on the solvent composition [3, 4]. We have therefore decided to carry out a new study of the acid-catalyzed methanolysis of polyvinyl acetate homopolymer and to compare it with that of some model compounds.

EXPERIMENTAL TECHNIQUES

Materials

Polyvinyl acetate was prepared by suspension radical polymerization at 50°C using azobisisobutyronitrile as initiator. Its limiting

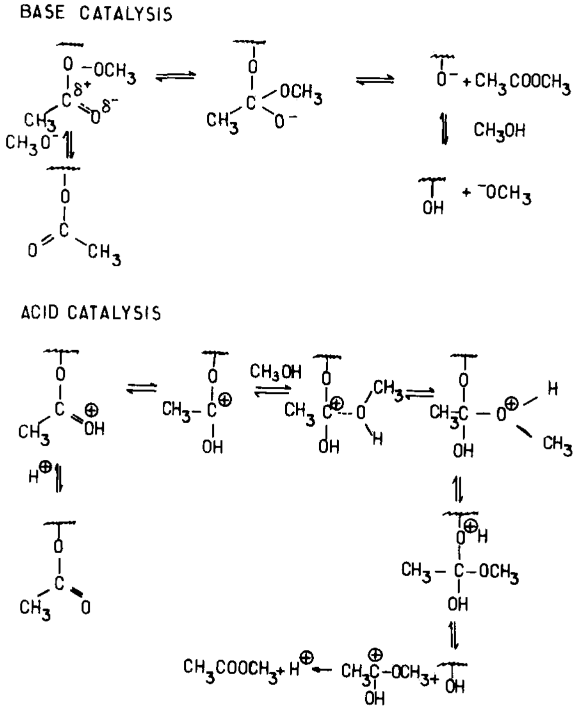


FIG. 1. Methanolysis mechanism: acid and base mechanisms.

viscosity number is 348 (25°C; solvent, acetone) which corresponds to an average molecular weight of $\overline{M}_n$ = 730,000 [5].

The simple alkyl acetates (ethyl, n-propyl, isopropyl, tert-butyl) were commercial products (Merck, Eastman). Diethyl carbinol acetate was prepared from diethyl carbinol and acetic anhydride in the presence of zinc chloride [6]. Triethyl carbinol acetate was obtained at moderate temperatures from triethyl carbinol and acetyl chloride in ether in the presence of dimethylaniline. Diacetopentane and triacetopentane were prepared according to the literature [7].

Methanolysis

Dried polymer was dissolved at a low concentration (about 1%) in the solvent [tetrahydrofuran (THF) or THF-methanol mixtures] 24 hr prior to the reaction and introduced into a glass vessel thermostated at 30°C. After thermal equilibrium was reached the catalyst (HCl in methanol) was added and the mixture thoroughly stirred. Sampling was carried out at chosen time intervals for chromatographic analysis or characterization studies.

Because of the retarding effect of water on acid-catalyzed methanolysis [4], the solvent were carefully dried before use (water content less than 1% or 1‰.

Kinetic data were obtained from gas chromatographic analysis of the methyl acetate produced, and compared to heptane added as an internal reference by using a calibration curve. The column was packed with carbowax (20%) on chromosorb and the analysis was carried out at 60°C.

Some secondary products were detected: methyl chloride from the esterification of HCl; formic acid and aldehyde from the oxidation of methanol; and probably $Cl(CH_2)_4OH$ from the opening of the THF ring. Their amounts were always small if the reaction temperature was kept at 30°C.

Hydrochloric Acid Concentration

It has been shown that the acidity of HCl is a function of the solvent mixture. A good example is given by the system ethanol-dioxane [4]. No data are available for the system THF-methanol. A series of mixtures has been studied by potentiometric titration of HCl (4×10^{-3} $\underline{N}$) with ammonium n-tetrabutoxide (0.1 $\underline{N}$). The concentrations were chosen so that there is practically no change in volume upon titration. A calibration curve was obtained from the potentiometric titration of a mixture of ClO_4Li (0.1 $\underline{N}$) and variable amounts of ClO_4H in the $THF\text{-}CH_3OH$ mixture saturated with H_2. The measurement electrode was platinated platinum and the reference electrode, calibrated from the

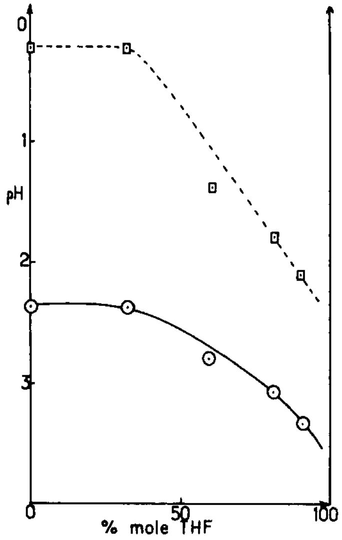


FIG. 2. Change of pH of a 0.04 N HCl solution as a function of the molar composition of the solvent mixture of methanol-tetrahydrofuran (THF) (——). Extrapolated curve for 0.6 N, HCl solution (--).

measurement of the half potential of the system ferricinium-ferrocene, was a silver electrode dipped in a solution of 0.1 M ClO_4Ag and 0.1 N ClO_4Li in the THF-CH_3OH mixture.

The results reported in Fig. 2 show that the acidity decreases at low methanol content. The HCl concentration used for methanolysis is much more higher and an extrapolation procedure must be used. However, the results are questionable because of the uncertainties, not only of the extrapolation procedure, but also due to the behavior of the reference chosen (ferrocene-ferricinium) in the solvents used. Thus the exact correction to be applied is not known and the value of the results reported is limited.

RESULTS AND DISCUSSION

The kinetic data for the methanolysis in various THF-CH_3OH mixtures are illustrated in Fig. 3. The initial rates, as well as the degrees of acceleration, are dependent on the composition of the solvent. The reaction scheme illustrated in Fig. 1 shows that the initial rate is dependent on the vinyl acetate unit $\{A\}$ concentration, $\{H^+\}$, and $\{CH_3OH\}$. The experiments have been carried out with

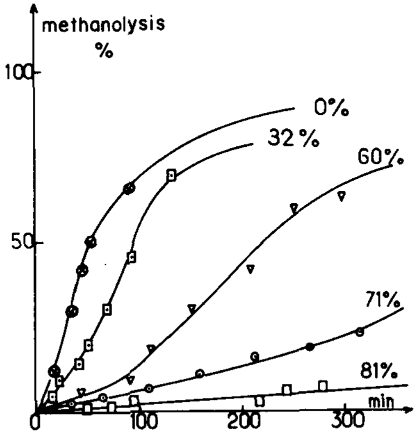


FIG. 3. Polyvinyl acetate methanolysis yield as a function of time for various THF contents (mole %) of the solvent mixture THF-methanol.

the same polymer concentration and the same HCl concentration. Although a correction is to be applied to $\{H^+\}$ at high THF content, and despite the data of Minsk, Priest, and Kenyon [1] and also of Texier et al. [3] concerning the order of the reaction versus $\{H^+\}$, it seems reasonable in a first approximation to assume a first order versus $\{H^+\}$. Therefore

$$V_0 = -\frac{d\{A\}}{dt} = k_0\{A\}_0\{H^+\}\{CH_3OH\}^{\alpha} = k_0'\{CH_3OH\}^{\alpha} \tag{1}$$

A plot of log V_0 vs log $\{CH_3OH\}$ (Fig. 4) shows a reasonable straight line, assuming that the reaction is first order vs $\{CH_3OH\}$. A larger deviation is observed for the mixture the richer it is in THF, and this is certainly caused by the neglect of the unknown correction to be applied to $\{H^+\}$. All the results, assuming $\alpha = 1$, are gathered in Table 1. The last column gives the results that take into account the correction for $\{H^+\}$, which is probably much too large.

Concerning the acceleration, which is also observed in the case of base catalysis, it has been proposed by Sakurada [8] to explain it by assuming three different rate constants according to the kind of triad concerned.

In these triads, noted respectively as AAA, OAA, OAO, the central A unit may be adjacent to 0, 1, or 2 vinyl alcohol units. Assuming $k_{AAA} < k_{OAA} < k_{OAO}$ and the initial concentration of OAO to be negligible,

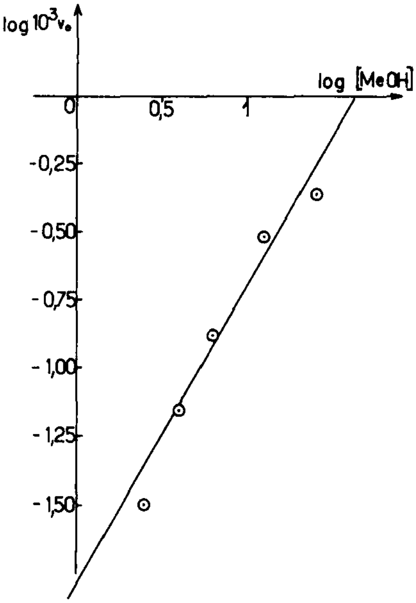


FIG. 4. Logarithmic plot of methanolysis rate vs methanol concentration.

Sakurada et al. [9] have given the rate equation

$$-\frac{d\{A\}}{dt} = k_0\{A\}\{OH^-\}\left[1 + (\alpha - 1)\frac{\{OAA\}}{\{A\}}\right] \tag{2}$$

where

$$\alpha = k_{OAA}/k_{AAA}$$

Sakurada et al. have also observed that the rate constant at time t, k_t, may be expressed by an empirical equation:

$$k_t = k_0\left(1 + m\,\frac{A}{A_0}\right) \tag{3}$$

TABLE 1. Methanolysis of Polyvinyl Acetate in Various Solvent Mixtures

Run	$\frac{\text{THF}}{\text{THF + MeOH}}$ (mole %)	{AO} (mole %)	{HCl} (mole %)	{MeOH} (mole/liter)	V_0 [mole/(1)(min)]	$k_0' \times 10^3$ [min/(mole)^2 (liter)$^{-2}$]	$k_0 \times 10^5$ [min/(mole)^2 (liter)$^{-2}$]	$k_0 \times 10^5$, corrected	m
I	0	0.120	0.640	25	0.43	3.60	14.5	14.5	36
II	32	0.120	0.640	12.5	0.30	2.50	20.0	20.0	26
III	60	0.119	0.645	6.20	0.129	1.08	16.90	169	18
IV	71	0.119	0.645	4.12	0.070	0.59	14.20	300	9
V	81	0.140	0.045	2.47	0.032	0.23	10.70	320	6

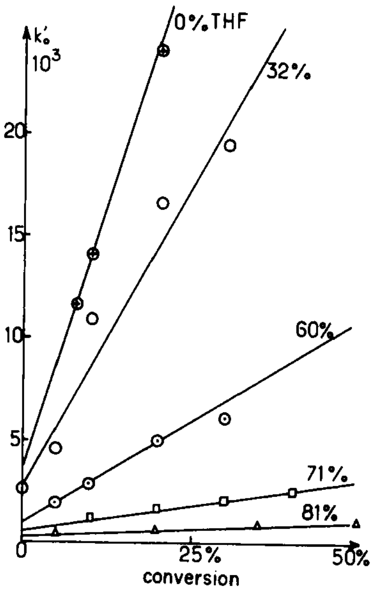


FIG. 5. Methanolysis rate constant as a function of conversion for various THF contents (mole %) of the solvent mixture THF-methanol.

where m is the empirical acceleration degree. The use of Eqs. (2) and (3) gives a relationship between α and m.

In the present case, plots of k_t vs A/A_0 (Fig. 5) give reasonably straight lines from which the acceleration degree m may be deduced. A plot of m vs the THF content of the solvent mixture (Fig. 6, Curve 1) also gives a good straight line.

For base catalysis, Sakurada [8] attributed the acceleration to the local concentration of the alkali around the polymer chain due to attraction by free hydroxyl groups. This statement has been challenged by Arranz and Ashraf [10], who have shown that m is not dependent upon the NaOH/ester ratio. They have also shown that m is not temperature dependent but depends on the composition of the solvent mixture. They have proposed that the acceleration is due to the formation of an hydrogen bond between a OH group of an hydrolyzed unit and the carboxyl group of an adjacent ester unit. The presence of hydrogen bonds has been proved by Nagai and Segane [11] using IR spectroscopy.

In order to test this idea, we have carried out a study with different model compounds in acid catalysis as well as in base catalysis for a few cases. The results, together with some of those of Sakurada, are

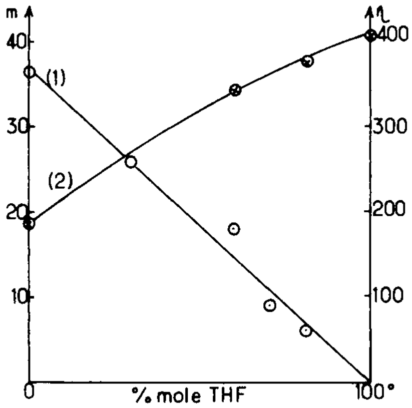
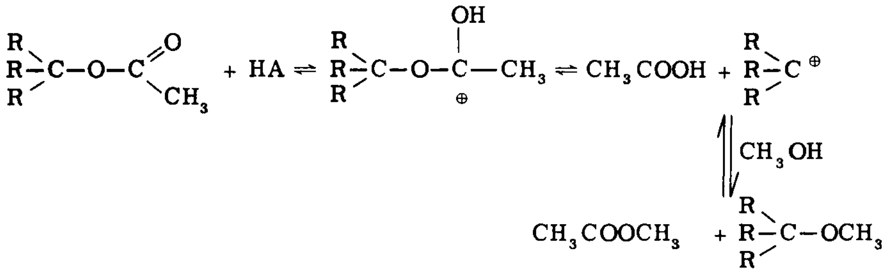


FIG. 6. Acceleration ratio m (Curve 1) and limiting viscosity number (Curve 2) as functions of the THF contents (mole %) of the solvent mixture.

reported in Table 2. It may be observed that in base catalysis the rate constants for isopropyl acetate, diacetopentane, and triacetopentane are rather close to that of the polymer. On the other hand, in acid catalysis the rate constant for the polymer is lower. Isopropyl acetate is a very bad model for the polymer; diethylcarbinol acetate is better. The high value for triethylcarbinol acetate is caused by the fact that the mechanism for tertiary alcoxy compounds is different from that for the primary or secondary ones illustrated in Fig. 1.

For tertiary compounds the mechanism [12] is



$$R_3C{-}O{-}C(=O)CH_3 + HA \rightleftharpoons R_3C{-}O{-}\overset{OH}{\underset{\oplus}{C}}{-}CH_3 \rightleftharpoons CH_3COOH + R_3C^{\oplus}$$

$$R_3C^{\oplus} \xrightleftharpoons{CH_3OH} CH_3COOCH_3 + R_3C{-}OCH_3$$

The main difference in the base and acid catalysis is that {CH$_3$OH} is rate determining in the latter. The limiting viscosity numbers data reported in Table 3 show that CH$_3$OH is a rather bad solvent for polyvinyl acetate, so that accessibility of the ester groups to CH$_3$OH

TABLE 2. Methanolysis of Model Compounds (30°C)

	Acid catalysis				Base catalysis			
Acetate units	{HCl} (mole %)	$\frac{\{\text{THF}\}}{\text{THF + MeOH}}$ (mole %)	$k_0 \times 10^2$	$k_0 \times 10^2$, corrected	{NaOH} (mole/liter)	Solvent	k_0 (mole/min^2)	Ref.
Ethyl	0.210	60	1.0	10	0.0172	Acetone 75 Water 25	3.5	5
n-Propyl	0.160	60	0.72	7.2				
Isopropyl	0.210	60	0.29	2.9	0.0172	Acetone 75 Water 25	0.57	5
tert-Butyl	0.210	60	0.161	1.61				
Diethyl-carbinol	0.160	60	0.078	0.78				
	0.160	81	0.081	3.20				
Triethyl-carbinol	0.160	60	0.51	5.7				
Polyvinyl	0.160	60	0.0169	0.169	0.0172	Acetone 75 Water 25	0.37	5
Diaceto-pentane	0.182	60	0.097	0.97				
Triaceto-heptane	0.182	60	0.120	1.20				

TABLE 3. Limiting Viscosity Numbers Data for Polyvinyl Acetate and Partially Hydrolyzed Polyvinyl Acetate in Various Solvent Mixtures

	Solvent	η_{sp} (g/cm^3)	k[a]	r[b]
Polyvinyl acetate	Acetone	348	0.542	0.999
	Methanol	188	0.587	0.999
	MeOH, THF (40% MeOH)	345	0.462	0.993
	MeOH, THF (10% MeOH)	374	0.609	0.999
	THF	402	0.616	0.999
Hydrolyzed polyvinyl acetate[c]	Methanol	232.4	0.546	0.996
c		327.0	0.462	0.994
c		361.0	0.614	0.999
d	Methanol	235	0.413	0.993
d		318.7	0.554	0.992
d		351.6	0.513	0.999

[a] Huggins coefficient.

[b] Statistical correlation coefficient.

[c] Partially hydrolyzed polyvinyl acetate (10%) prepared in pure methanol.

[d] Partially hydrolyzed polyvinyl acetate (>15%) prepared in a mixture (methanol, THF) with 19% mole MeOH.

may be limited. If the solvent does contain THF, the chain expansion is better, so that although there is certainly a preferential solvation by THF, the accessibility to CH_3OH may increase at first. Thus the increase of corrected k_0 reported in Table 1 for moderate proportions of THF may be understood although the correction is certainly overestimated for high THF content.

Concerning acceleration, the kinetic curves in Fig. 7 for models with two or three acetate groups show no acceleration in base catalysis and low values of m (1.2 and 1.7, respectively) in acid catalysis. Intramolecular hydrogen bonds have been shown in the case of diacetopentane. The carbonyl band of pure diacetopentane is at 1735 cm^{-1}; in the case of partial methanolysis this band is present together with another one at 1715 cm^{-1}. The ratio of the intensities of the bands is not changed upon a fiftyfold dilution in methanol or in butanol. Thus the 1715 cm^{-1} band may be assigned to carbonyl groups with intramolecular hydrogen bonds.

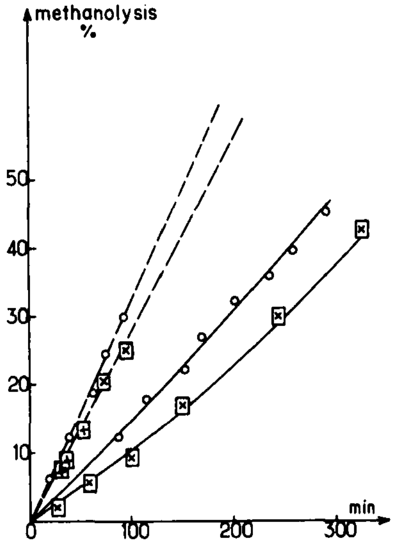
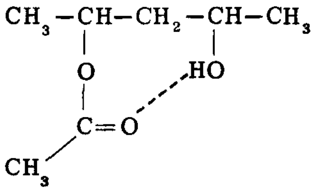
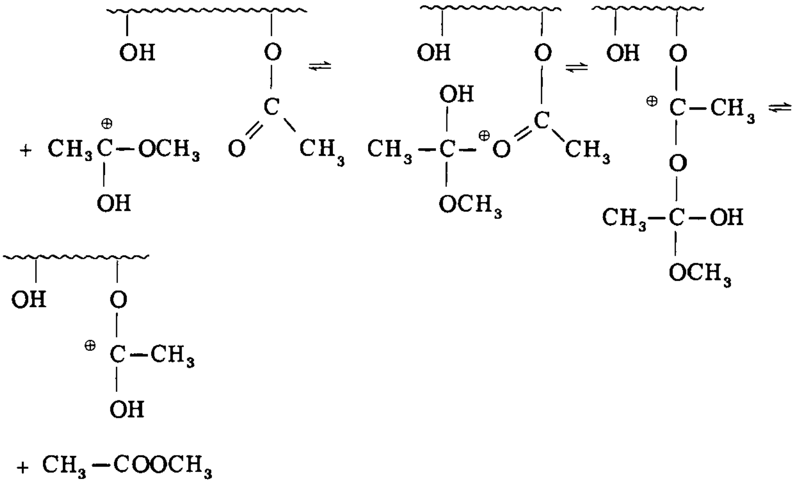


FIG. 7. Model compounds diacetopentane (A_c2) (×) and triacetoheptan (A_c3) (○) methanolysis yield vs time for acid catalysis (——) (HCl: 0.182 N; THF 60 mole %; methanol 40 mole %) and base catalysis (--) ($\{OH^-\}$ = 0.0062 N in methanol).



Despite the presence of hydrogen bonds, the methanolysis rate of the di- and triacetate model compounds is only a little higher than that of diethylcarbinol. Therefore the hydrogen bonds between an acetate group and an adjacent OH group are not a sufficient condition to cause large acceleration degrees such as those observed in the case of polyvinyl acetate. It is more interesting to look at Curve 2 of Fig. 6 where the reverse correlation between the values of m and the expansion of the chain as a function of the composition of the solvent mixtures is shown. Acceleration is enhanced by a closer coiling of the chain. Looking again at the methanolysis mechanism, it may be observed that in both the cases of acid and base catalyses, the last step of formation of the OH group involves the release of the ion that was active for the first step of the process. If the chain is expanding, this ion may rapidly diffuse in the solvent, but if the chain is more tightly coiled, the ion may be trapped in the coil and may readily attack an adjacent carbonyl group. Thus the acceleration might be visualized as a progressive trapping of the catalyst ion by the coiled macromolecules. More precisely, it may be tentatively proposed that in a coiled macromolecule the ion released by the penultimate step of the acid catalysis mechanism, namely $CH_3-C^{\oplus}(OH)(OCH_3)$, directly attacks an adjacent carbonyl group before releasing methyl acetate and a proton. After an initiation step, the propagation of the methanolysis in the chain would involve the mechanism



Finally, it is to be noted that the hydrodynamic volume of the chain progressively changes during methanolysis. At a high degree of conversion, precipitation occurs, probably due to the association of OH groups. This finally leads to semicrystalline polyvinyl alcohol. Before that, one may observed either a little expansion (see Table 3 for pure methanol) or, if the solvent does contain THF, a progressive coiling.

ACKNOWLEDGMENT

The authors are grateful to Dr. M. Breant for her support in the determination of hydrochloric acid concentration in THF-CH_3OH mixtures.

REFERENCES

[1] L. M. Minsk, W. J. Priest, and W. O. Kenyon, J. Amer. Chem. Soc., 63, 2715 (1941).

[2] J. R. Roberts and M. C. Caserio, Chimie Organique Moderne, Ediscience, Paris, 1968.

[3] F. Texier, J. Guenzet, and B. Merah, C. R. Acad. Sci., Paris, C, 275, 339 (1972).

[4] E. A. Braude and E. S. Stern, J. Amer. Chem. Soc., 70, 1976 (1948).

[5] R. H. Wagner, J. Polym. Sci., 2, 21 (1947).

[6] R. H. Baker and F. G. Badwell, Org. Syn. Coll., 1955, 141.

[7] V. Chytry, B. Obereigner, and D. Lim, Eur. Polym. J., 9, 493 (1973).

[8] I. Sakurada, Pure Appl. Chem., 16, 263, 1968.

[9] I. Sakurada, Y. Sakaguchi, and S. Ishiguro, Chem. High Polym., Tokyo, 13, 441 (1956); 17, 115 (1960).

[10] F. Arranz and M. Ashraf-Tahir, Rev. Plast. Mod., 160, 1 (October 1969).

[11] E. Nagai and N. Segane, Chem. High Polym., Tokyo, 12, 195 (1955).

[12] T. A. Geisman Principes de Chimie Organique, Dunod, Paris, 1965, p. 158.

Accepted by editor April 2, 1974
Received for publication April 10, 1974