Investigations on the Stereochemistry and Polymerization of 1,3-Dioxolane Derivatives. 7. Influence of the Configuration of Di- and Trisubstituted Dioxolanes on the Rate of Hydride Transfer in the Reaction with Ph_3CSbCl_6

Z. Jedliński,* J. Lukaszczyk, J. Dudek, and M. Gibas

Institute of Polymer Chemistry of the Polish Academy of Sciences, Zabrze, Poland and the Department of Polymer Chemistry, Technical University, Gliwice, Poland.

Received December 15, 1975

ABSTRACT: The rate of hydride transfer and formation of corresponding 1,3-dioxolan-2-ylium salts in the reaction of 1,3-dioxolane and its isomeric di- and trisubstituted derivatives with triphenylmethyl hexachloroantimonate in CH_2Cl_2 and CH_3NO_2 has been studied. The enthalpy and entropy of activation of these reactions also have been calculated. The results show that the hydride ion transfer is strongly dependent not only on the type of substituents at the 1,3-dioxolane ring, but also on their stereochemical configuration. For *cis*-4,5-dimethyl isomers this reaction is considerably faster than for their corresponding trans isomers. The data obtained are discussed with respect to the basicity and chemical shift of H(2) of corresponding isomeric dioxolane derivatives.

The studies on the initiation mechanism in the polymerization of 1,3-dioxolane (1) carried out in the presence of triphenylmethyl salts have received considerable attention recently.[1–3]

It was stated that in the first step of initiation, there takes place a hydride transfer from 1,3-dioxolane (1) to the carbenium cation of the dissociated triphenylmethyl salt. Dioxolenium salt formed in such a manner can initiate a polymerization, but can also decompose producing β-chloroethyl formate (Figure 1). Kubisa and Penczek[4,5] have observed that the stability of dioxolenium salts depends very much on the structure of the anion.

Taking into account the investigations made so far in this field, hydride transfer reactions are known to be very important for the understanding of the initiation process in the polymerization of certain heterocyclic compounds. This reaction is considered to be one of the main, elementary reactions taking place in the initiation step of the polymerization of 1,3-dioxolane and its derivatives by triphenylcarbenium or triethyloxonium salts.[3] Therefore many papers have been concerned with this process, a number of such essential parameters as the kind of initiator, solvent, temperature, concentration of reagents, nature of ions (free ions, ion pairs) being taken into account. However, little attention has been paid to the influence of the steric effect, i.e., the stereochemical structure of cyclic monomers and dioxolenium ions, on the course of polymerization. Thus it is known that in ionic polymerization processes of vinyl and diene monomers the steric effects are of great importance.[6]

It is known from the earlier published literature data that the 1,3-dioxolane derivatives with alkyl substituents in the positions 4,5 are considerably less reactive in the cationic polymerization as compared with unsubstituted 1,3-dioxolane.[7,8]

In our previous paper we have shown that in the case of trisubstituted dioxolanes existing in various isomeric forms (Figure 3) the overall rate of polymerization in the presence of $BF_3 \cdot Et_2O$ is influenced by the steric configuration of monomers.[9]

It might be supposed that the observed influence of substituents, on the reactivities of the substituted isomeric dioxolanes, is due to the differences existing in the structure and rates of formation of active species produced from various isomers.

To test the validity of that assumption we have undertaken studies on the influence of the isomerism of 1,3-dioxolane derivatives on the rate of hydride transfer and the formation of the appropriate dioxolenium salts. A number of substituted 1,3-dioxolanes obtained from butanediol-2,3 and having a general formula given below were chosen as model compounds (Figure 2). Triphenylmethyl hexachloroantimonate (7) was applied as a catalyst.

4,5-Disubstituted-1,3-dioxolane derivatives may occur in two isomeric forms (trans and cis), while the 2,4,5-trisubstituted derivatives exist in three stereoisomeric forms (trans, cis-syn, and cis-anti) (Figure 3).

Model compounds of this kind are particularly convenient for studying the initiation process since many of them do not polymerize under the chosen reaction conditions (excluding 6) and the reaction may hence be stopped at the hydride transfer step when the corresponding dioxolenium ions are formed. This fact facilitates the investigation of the reaction mechanism in the preliminary step of the initiation process.

Results and Discussion

(a) Rate of Hydride Transfer. The isomeric acetals react with 7 with the transfer of the hydride ion giving the corresponding dioxolenium salts and triphenylmethane. The colored cation Ph_3C^+ disappears as a result of this reaction and the spectrophotometric method can be used to follow the course of this process. It should be noticed that at low concentration below 10^{-4} mol $l.^{-1}$ the triphenylmethyl salt is almost fully dissociated into free ions.[1,3]

Rate of the hydride transfer and of the formation of dioxolenium salt depends not only on the kind of substituent at the carbon C(2), but also on the steric configuration of the acetal used. The rates of formation of the dioxolenium salt from the trans isomers of the substituted dioxolanes are listed in Table I in order to show the influence of the substituent especially at C(2).

The data contained in Table I show that methyl groups at positions 4,5 accelerate the hydride transfer reaction when compared with unsubstituted dioxolane. Substituents at C(2) generally retard the rate of this reaction, and that effect is more evident for bulkier substituents. In nitromethane the reaction is slower than in dichloromethane.

The results of spectroscopic measurements also show that for both isomers the rate of hydride transfer and the formation of the dioxolenium salt correlates closely with the δH(2) which depends to a large extent on electron density at the site of C(2)

---

* Institute of Polymer Chemistry of the Polish Academy of Sciences.

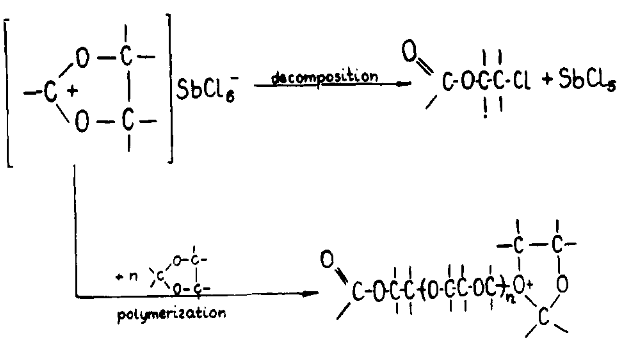

Figure 1. Scheme.

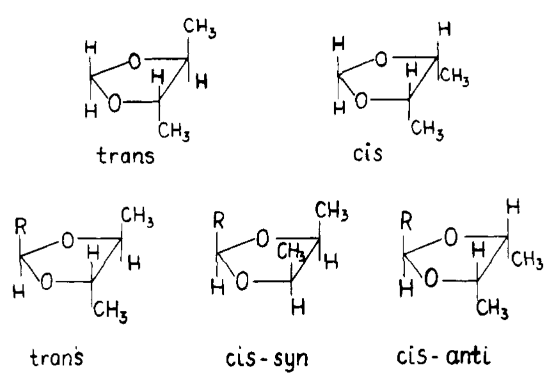

Figure 3. Formulas of stereoisomers.

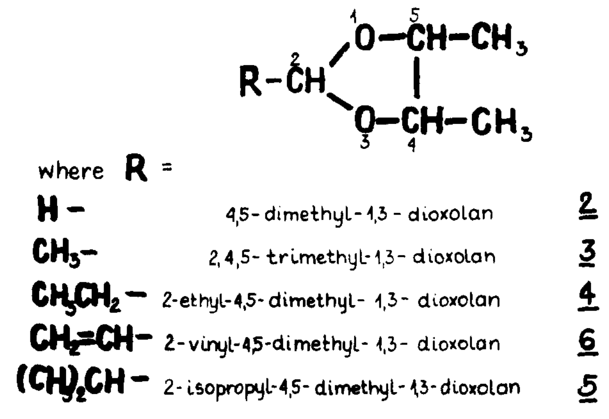

Figure 2. Formulas.

to which the proton is bonded. This chemical shift and also the basicity (pK_b) for 1,3-dioxolane derivatives depends on the steric arrangement of substituents.

In Table II are summarized the data calculated from spectrometric measurements for various isomers: rate constants for the reaction of the formation of dioxolenium salts as a result of the hydride ion transfer, thermodynamic parameters for that reaction as well as data illustrating the correlation between the basicity and the chemical shift of protons at C(2) on the one hand, and the configuration of particular substituted isomeric acetals on the other. Data contained in Table II show that the trans isomers of substituted dioxolanes are generally weaker bases than the corresponding cis isomers. In the NMR spectra the signals of H(2) protons of the trans isomers are downfield shifted in relation to those of the cis-syn configuration. The only exception is the **2** having two H(2) protons, which have different chemical shifts in the cis isomer (Table II).

In relation to the corresponding cis-syn isomer the downfield shift of the H(2) signal in the trans isomer may indicate a lower electron density at the H(2) in the latter which should decrease the susceptibility for the attack of the triphenylmethyl carbenium ion and also the rate of the hydride ion transfer.

The downfield shift of H(2) is due to the deshielding effect of CH_3(4) which is on the same side of the dioxolane ring as the H(2) proton.[10]

In the cis-syn isomers the H(2) proton (in *cis*-**2** one of the protons) is on the opposite side of the ring with respect to the CH_3(4,5) and therefore is not deshielded by those groups. Kinetic investigations confirmed that the trans isomers react therefore slower than the corresponding cis isomers.

The enthalpy of activation for the trans isomers of the 2,4,5-trisubstituted dioxolane derivatives is smaller than that for the cis-syn isomers. The cis isomer of **2** is a particular case as it has at C(2) two hydrogen atoms differing from each other in their chemical shifts. One may therefore expect that in the *cis*-**2** for one H(2) the enthalpy of activation of hydride transfer will be smaller, and for the second H(2) it will be greater than that found for equivalent H(2) protons of the *trans*-**2**.

(b) Properties of the Isomeric Dioxolenium Salts. The reaction of hydride transfer in the case of **1** is accompanied by further reactions leading to the polymerization or the deactivation of the dioxolenium salt. We have studied this reaction by observing the changes in the NMR and ir spectra of the reaction mixtures: **7**, acetal in dichloromethane or nitromethane. A typical NMR spectrum of the *trans*-**2** with **7** in nitromethane solution is presented in the Figure 4.

In this spectrum one can observe the disappearence of signals of the Ph_3C^+ cation in the range 7.5–8.5 ppm, the reduced intensity of the H(2) signal at δ = 4.79 ppm, and the reduced intensity of the signals H(4,5) and CH_3(4,5) of the acetal. New signals appear, however, at $\delta \cong 9.3$ ppm and $\delta \cong 1.87$ ppm,

Table I
The Spectrometric Data and Rate Constants of H^- Transfer from Trans Isomers of 1,3-Dioxolane Derivatives to the Ph_3C^+ Cation

Compd No.	R(2)	R(4,5)	Solvent	δH(2) from HMDS, ppm	296 K, $k^{+}_{H^-} \times 10^3$, mol l.$^{-1}$ s^{-1}
1	H	H	CH_2Cl_2	4.74	7.71
2	H	CH_3	CH_2Cl_2	4.83	41.36
2	H	CH_3	CH_3NO_2	4.79	32.28
3	CH_3	CH_3	CH_2Cl_2	5.02	12.93
4	CH_3CH_2	CH_3	CH_2Cl_2	4.89	15.06
6	$CH_2{=}CH$	CH_3	CH_2Cl_2	5.21[a]	23.09
5	$(CH_3)_2CH$	CH_3	CH_2Cl_2	4.78	1.75
5	$(CH_3)_2CH$	CH_3	CH_3NO_2	4.64	0.98

[a] Measured in CCl_4.

Table II
Rate Constants and Activation Parameters of the H^- Transfer from Dioxolane Derivatives to the Ph_3C^+ Cation

Compd No.	R(2)	R(4,5)	Isomer	$k_{\mathrm{H}^-}{}^+ \times 10^3$ 296 K, mol $\mathrm{l.}^{-1}\,\mathrm{s}^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, kcal mol^{-1}	$\mathrm{p}K_b$	δH(2) in CCl_4, ppm
2	H	CH_3	Trans	41.36	12.6	−22.0	7.49	4.83
2	H	CH_3	Cis	73.5	11.7	−23.9	7.48	4.65; 4.95
3	CH_3	CH_3	Trans	12.93	10.6	−31.1	7.58	5.02
3	CH_3	CH_3	Cis-syn	34.08	11.0	−28.1	7.58	4.87
4	CH_3CH_2	CH_3	Trans	15.06	9.1	−36.0	7.65	4.86
4	CH_3CH_2	CH_3	Cis-syn	35.07	9.5	−33.1	7.24	4.69
5	$(CH_3)_2CH$	CH_3	Trans	1.75	10.9	−34.2	7.78	4.64
5	$(CH_3)_2CH$	CH_3	Cis-syn	5.5	11.6	−29.5	7.44	4.48
1	H	H		7.71	15.6	−15[a]	7.75	4.75

[a] From ref 3.

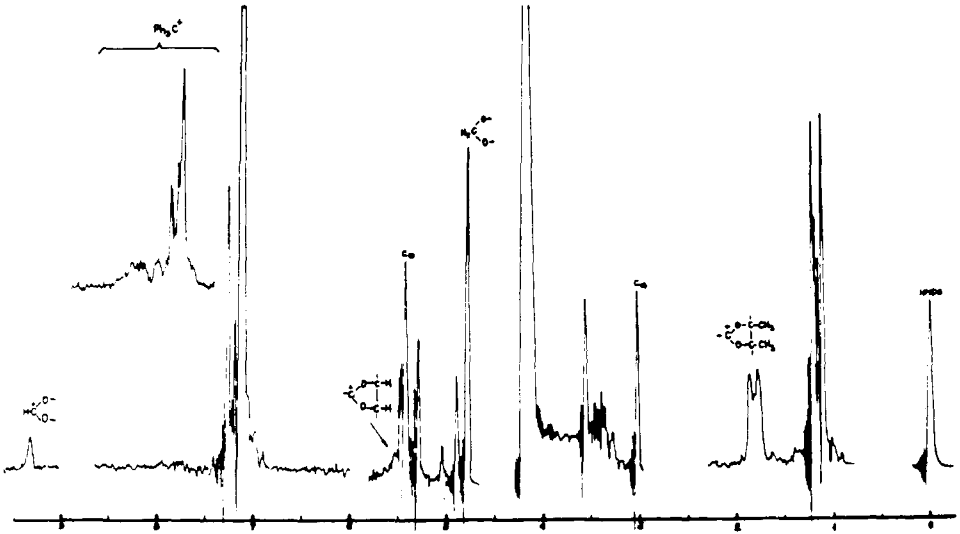

Figure 4. The NMR spectrum of the reaction mixture 4,5-dimethyl-1,3-dioxolane (**2**)–Ph_3CSbCl_6 (**7**) in CH_3NO_2.

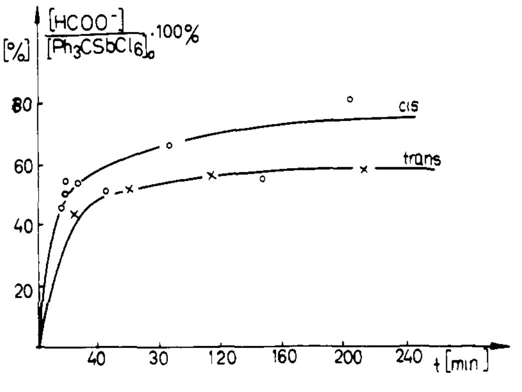

Figure 5. Changes in the amount of the formate formed in the system *trans*- or *cis*-4,5-dimethyl-1,3-dioxolane (**2**)–Ph_3CSbCl_6 (**7**) in CH_2Cl_2 solution.

which may be assigned to H(2) and CH_3(4,5) protons of the 4,5-dimethyl-1,3-dioxolane-2-ylium cation. These new signals did not disappear in nitromethane (up to 5 h) so that the decomposition of dissociated salt does not occur.

In dichloromethane, which has a significantly lower dielectric constant, one can observe a relatively fast decomposition of the dioxolenium salt with the formation of the respective formate.

In the NMR spectrum an additional signal of the formate methine proton then appears (at 8.5 ppm); a strong band at 1733 cm^{-1} (carbonyl) can be seen in ir spectrum. Based on the NMR spectra we have calculated as a function of time the change of the content of the monomer, catalyst, and reaction products in the reaction mixture.

Decomposition reactions of the salts of **2** having cis configuration are similar to those of the trans isomer, but the rates of these reactions are different. The dioxolenium salt formed from the cis isomer decomposes producing the corresponding formate faster than the salt from the trans isomer. This is shown in Figure 5. Thus not only the rate of formation but also the stability of the dioxolenium salts formed depend on the configuration of the stereoisomers of individual substituted dioxolanes.

2,4,5-Trisubstituted dioxolane derivatives behave differently than **2**. As a result of the hydride ion transfer the former give relatively stable dioxolenium salts. The NMR and ir spectra of the reaction mixture of trisubstituted acetal **7** in nitromethane or dichloromethane taken even after several hours do not show any signals or bands characteristic of ester groups, as observed in the case of the **2** isomers. It is possible to separate these salts in a crystalline form.[13]

Dioxolenium salts of the di- and trisubstituted derivatives of 1,3-dioxolane initiate the polymerization of **1**.

The regularities observed by us indicate that the initiation step of the polymerization occurring with the hydride ion transfer and the formation of a flat carbenium ion depends to a certain extent on the dimensions of the substituent at

C(2). However, this steric factor does not limit the formation of active centers, i.e., dioxolenium ions. Steric hindrance, however, may be the decisive factor in the next stages of the process; i.e., it can restrain the propagation step. Attack of the carbenium ion on the monomer with a bulky substituent at C-2 may be hindered. Probably it is the reason for the difficulties found in the polymerization of the di- and trisubstituted dioxolanes.

Conclusions

When examining the initiation process in the polymerization of **1** and its derivatives by triphenylmethyl salts one should take into account the rate of the hydride ion transfer reaction from the monomer to the triphenylmethyl cation, and the stability of the dioxolenium salt formed. The experimental data presented above show that the H^- transfer reaction is the fastest for the *cis*-**2**. For some 2,4,5-trisubstituted derivatives, and especailly for the cis-syn isomers, this reaction is considerably faster than that typical for the unsubstituted dioxolane. The stereoisomerism of monomers thus has a significant influence on the rate of the hydride ion transfer and on the rate of the first step of the initiation reaction.

Dioxolenium salts of the di- and particularly of the trisubstituted dioxolanes are considerably more stable than those derived from **1**. When comparing these results with the polymerizability of these compounds (**1** polymerizes; **2** as well as trisubstituted dioxolanes give only the corresponding dioxolenium salts), it may be supposed that hydride transfer is not the limiting factor in the polymerization of substituted dioxolanes. It is therefore concluded that further primary processes are responsible for chain propagation.

Experimental Section

Solvent and Reagents. Solvents CH_2Cl_2 and CH_3NO_2 were purified according to the procedure generally used in ionic processes. *meso-* and *dl*-butanediol-2,3 were obtained by fractionation on a high-efficiency packed column from the commercial butanediol-2,3 which was a mixture of both possible forms. The obtained fractions were: *d,l*, bp 88–89 °C (17.5 mm); meso, bp 95–96 °C (17.5 mm).

Monomers. The 2,4,5-trisubstituted 1,3-dioxolanes (2-methyl- (**3**) 2-ethyl- (**4**), 2-isopropyl- (**5**), and 2-vinyl-4,5-dimethyl-1,3-dioxolane (**6**)) (Figure 2) were obtained by the Fischer azeotropic procedure[10] in the reaction of butanediol-2,3 and the corresponding aldehyde in the presence of a small amount of *p*-toluenesulfonic acid as a catalyst. In the case of the saturated derivatives, 1,3-dioxolane aldehyde and butanediol were used in chemically equivalent amounts; for **6** it was necessary to use a slight excess of aldehyde (1,1:1) as previously described.[9] Benzene or methylene chloride (for the lower boiling acetals) were used as azeotropic agents.

4,5-Dimethyl-1,3-dioxolane (**2**) and 1,3-dioxolane (**1**) were prepared as described by Astle,[12] i.e., by heating *p*-formaldehyde with an excess of the corresponding glycol in the presence of Amberlite IR-120 resin as a catalyst. The trans isomers of acetals were obtained from the *d,l* form of butanediol-2,3. The cis isomers were prepared from the meso form. In the case of 2,4,5-trisubstituted acetals, the cis-syn isomer with an admixture of cis-anti isomer was obtained. By distillation on a highly efficient column it was possible to isolate pure cis-syn isomers which contained below 5% of the cis-anti form.

The acetals were dried by distillation over Na or an alloy of Na and K under reduced pressure of nitrogen, and kept in dry ampules under nitrogen.

The properties of acetals used are given in Chart I.

Chart I

Acetal	bp, °C	$n^{25}D$	Acetal	bp, °C	$n^{25}D$
1	74–75	1.4001	*trans*-**4**	126–127	1.4032
trans-**2**	97	1.3980	*cis*-**4**	129–132	1.4091
cis-**2**	103–104	1.4060	*trans*-**5**	140	1.4080
trans-**3**	102–103	1.4011	*cis-syn*-**5**	148–150	1.4150
cis-**3**	108–108.5	1.4036	*trans*-**6**	49–50 (37 mm)	1.4192
			cis-syn-**6**[a]	56 (37 mm)	1.4258

[a] With an admixture of cis-anti form

Initiator. Triphenylmethyl hexachloroantimonate ($Ph_3C^+SbCl_6^-$ **7**) was prepared from Ph_3CCl and $SbCl_5$ by mixing equal volumes of 1 M solutions of these substrates in benzene (dried over P_2O_5 in a closed cycle). The precipitated salt was filtered off, washed several times with benzene, and dried in a vacuum desiccator.

Dioxolenium salts were obtained by adding to the solution of **7** in CH_2Cl_2 or CH_3NO_2 an equivalent amount of the respective isomers of acetals. The dioxolenium salt from the *trans*-**5** precipitated from CH_2Cl_2 solution without the addition of the precipitant; the other salts were precipitated by *n*-heptane, washed several times with *n*-heptane, and dried in vacuo.

Spectrometric Measurements. Rate constants of the hydride ion transfer were determined by measuring the decrease of the intensity of absorption at 430 for systems: **7** (10^{-4} mol l.$^{-1}$)–acetal (10^{-1} mol l.$^{-1}$) in CH_2Cl_2 or CH_3NO_2. All measurements were made under isothermal conditions using a Spekol spectrometer (Zeiss Jena) equipped with the EK-5 unit. The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated from the temperature dependence of the rate constant determined in the range 5–30 °C employing known Arrhenius and Eyring equations.

Ir spectra were taken on UR-120 (Carl-Zeiss Jena) apparatus.

The pK_b values of acetals were determined by Gordy's method.[13] The following proportions used were: 0.02 ml of MeOD for 1 ml of benzene and 0.02 ml of MeOD for 1 ml of acetal. The position of the OD band was measured in relation to the polystyrene band at 2850.7 cm^{-1}.

The spectra of reaction mixtures were made in 0.06-mm NaCl cells.

NMR spectra were taken using a Japan Electron Optics Lab. Model JNM-C-60H NMR spectrometer. HMDS or TMS was used as an internal standard.

References and Notes

(1) M. P. Dreyfuss, J. C. Westfahl, and P. Dreyfuss, *Macromolecules*, **1**, 437 (1968).
(2) O. A. Plechova, V. V. Ivanov, and T. I. Prokofeva, *Vysokomol. Soedin. Ser. A*, **16**, 14 (1973).
(3) S. Penczek, *Makromol. Chem.*, **175**, 1217 (1974).
(4) P. Kubisa and S. Penczek, *Makromol. Chem.*, **144**, 169 (1971).
(5) P. Kubisa, *Polimery*, **18**, 15 (1973).
(6) M. Szwarc, "Ions and Ion Pairs in Organic Reactions", Vol. 2, Wiley-Interscience, New York, N.Y., 1974.
(7) M. Okada, *Makromol. Chem.*, **80**, 196 (1964).
(8) Z. Jedliński and J. Lukaszczyk, *Makromol. Chem.*, **114**, 226 (1968).
(9) Z. Jedliński and J. Lukaszczyk, *Macromolecules*, **8**, 700 (1975).
(10) E. Willy, G. Binsch, and E. L. Eliel, *J. Am. Chem. Soc.*, **92**, 5394 (1970).
(11) R. Fischer and C. W. Smith, *J. Org. Chem.*, **26**, 319 (1960).
(12) M. J. Astle, J. A. Zaslowsky, and P. G. Lafyatis, *Ind. Eng. Chem.*, **46**, 787 (1954).
(13) W. Gordy and Sc. Stanford, *J. Chem. Phys.*, **7**, 93 (1939); **8**, 170 (1940); **10**, 204, 215 (1941); also J. Furukawa and K. Tada, "Ring Opening Polymerization," K. C. Frisch and S. L. Reegen, Ed., Marcel Dekker, New York, N.Y., 1969.
(14) Z. Jedliński, J. Dudek, J. Lukaszczyk, and M. Gibas, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, submitted for publication.