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Polymerization of 2-Methyloxacyclobutane with Triethyloxonium Ion Initiator

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SUMMARY

The polymerization of 2-methyloxacyclobutane in CH_2Cl_2 using Et_3OPF_6 as initiator yields high molecular weight polymers in high yields at low temperatures down to - 80°C. The rate of initiation is slow and the concentration of propagating oxonium ions so low that phenyl end-capping could not be used in a kinetic study. The polymerization is 2nd order in monomer in accordance with a scheme involving spontaneous termination. Chain irregularities of the head-to-head, tail-to-tail types are in this system found to be determined only by the polymerization temperature.

INTRODUCTION

Recently we investigated the structural aspects of the ring-opening polymerization of 2-methyloxacyclobutane (2-MOCB)(KOPS et al., 1980b). The polymerization yields a high proportion of head-to-head, tail-to-tail structures which increases with the polymerization temperature. It was found by ^{13}C NMR analysis of the tactic triads that propagation occurs in a random fashion from the mixture of enantiomeric monomers. Generally, higher molecular weights were obtained with the initiator Et_3OPF_6 than with PF_5 in the temperature range -78 to 0°C, although the $\bar{M}_n$ values were less than 10.000.

Now we wish to report a more detailed polymerization study utilizing the oxonium salt initiator and we have been able to obtain polymers with molecular weights which are more than an order of magnitude higher than the previous values. The polymerization of oxacyclobutane (oxetane) and the derivatives with substituents in the 3-position have been thoroughly investigated (SAEGUSA et al.,1973, BLACK and WORSFOLD, 1976) and also the oligomerization accompanying these polymerizations (DREYFUSS and DREYFUSS, 1976, GOETHALS, 1977, BUCQUOYE and GOETHALS, 1977). Surprisingly, however, very little

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work has been carried out concerning the polymerization of 2-MOCB after the original publication by ROSE, 1956 regarding the polymerizability. The structural features of the polymerization of 2-MOCB also warrents further investigation since in principle the polymers may be obtained with a highly regular structure (KOPS 1980a). It is only very recently that control of the chain propagation was obtained with coordination catalyst giving a predominant head-to-tail structure, however,the degree of stereospecificity in the case of a chiral monomer was small (OGUNI and HYODA, 1980).

EXPERIMENTAL

Materials: 2-MOCB was prepared as previously described (KOPS et al., 1980b). CH_2Cl_2, Et_3OPF_6 and NaOPh/THF were purified and prepared according to previously published procedures (HVILSTED and KOPS, 1979).

Polymerization Procedures: A high vacuum technique was applied using storage burets with Rotaflo valves and phials for adding solvents and reagents as described in detail elsewhere (HVILSTED and KOPS, 1979). Particular care was taken in purifying the monomer prior to use by distillation from K-Na alloy. Also the Et_3OPF_6 was dried very carefully in vacuum prior to contacting it with CH_2Cl_2 and monomer.

Termination with NaOPh was performed by using a phial technique in case of the attempted quantitative determination of the concentration of propagating oxonium ions by the end-capping technique (SAEGUSA and MATSUMOTO, 1968). In the other polymerizations the NaOPh was also used as termination reagent, however, prepared under N_2 in a dry box and applied with a syringe. The work-up of the polymers in the latter case was done by washing with 1N NaOH and water after dilution with CH_2Cl_2. After drying over Na_2CO_3 the solvent was evaporated and the polymer dried in vacuum (1 mbar) at 50°C.

Apparatus: Molecular weights were determined by GPC in THF solution using a Waters Model 200 instrument with polystyrene gel columns with porosities 10^6, $2 \cdot 10^4$, 10^4 and 10^3 Å. The molecular weight values were calculated from a calibration curve based on extended chain lengths for polystyrene and applying a Q-value of $15.6\ g \cdot mol^{-1} \cdot Å^{-1}$. The UV-measurements were performed in CH_2Cl_2 solution at room temperature in the range 225-325 nm on a Beckman DK-2A spectrophotometer. The ^{13}C NMR spectra were obtained on Bruker WH90 and HX270 Fourier transform spectrometers operating at 22.63 and 67.89 MHz respectively. The measurement were performed on 10% polymer solution in $CDCl_3$ with TMS as internal standard.

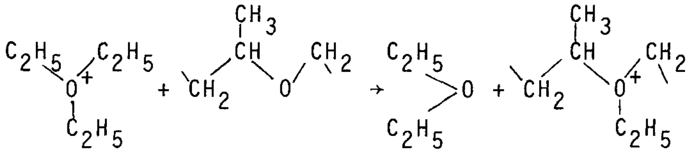
RESULTS AND DISCUSSION

With the objective of calculating rate constants in a kinetic study of the polymerization of 2-MOCB attempts were made to determine the concentration of active propagating oxonium ions by phenoxyl end-capping (SAEGUSA and MATSUMOTO, 1968) as we have done in case of other polymerizations (HVILSTED and KOPS, 1979).

The polymerizations were carried out in CH_2Cl_2 solution generally with an initial monomer concentration close to 1.68 $mol \cdot l^{-1}$, and a concentration of initiator around $2.7 \cdot 10^{-3}$ $mol \cdot l^{-1}$, although one experiment was carried out with a much higher concentration of initiator. Polymerization rates were studied in the temperature range -20 to -80°C and the data are presented in Table 1.

The experiments were first carried out at -20°C, however, it was found that the polymerization proceeds quite fast at that temperature, since 73% conversion is reached within 30 min. A more convenient temperature for a kinetic study is -50°C where the conversion reached only 13% during the same time interval. In that case the influence of the initial start-up period, during which the polymerization temperature is approached is decreased.

The determination of the phenoxyl group concentration shows, however, that although the total phenoxyl group concentration corresponds quite well to that of the charged initiator at the $2.6 \cdot 10^{-3}$ $mol \cdot l^{-1}$level, little or any of these phenoxyl groups are found to be at the ends of the polymer chains up to high conversions and reaction times. Even when the initiator concentration is increased more than 20-fold only a very small concentration is found after 121 minutes of reaction time at -50°C. At this high concentration of initiator the solubility becomes marginal as evidenced by a cloudiness in the polymer solution and it is not surprising that some deviation is found between the determined total concentration of phenoxyl groups and the amount of charged initiator. Only after a very long reaction time at -50°C, at the low concentration of initiator, it appears that a measurable amount of polymer bound phenoxyl groups is present. However, this is only a single experiment and in any case it certainly appears that in the early stages of the polymerization the concentration of propagating oxonium ions that could be detected is very small. In the latter stages the possibility exists that an exchange reaction between unreacted initiator and polymer takes place:



(1)

TABLE 1

Polymerization of 2-MOCB at Different Temperatures[a)]

			GPC		UV	
Temp. °C	React. time min.	Yield of pol. wt.%	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w \cdot 10^{-3}$	Total phenoxyl[c)] mol $\cdot \ell^{-1} \cdot 10^3$	Active ends[d)] mol $\cdot \ell^{-1} \cdot 10^3$
- 20	30	73	19	11	2.8	~ 0
	92	89	45	28	2.4	~ 0
- 30	60	71	45	101	-	-
	151	90	22	84	-	-
	360	93	22	81	-	-
- 50	30	13	20	53	-	-
	75	33	12	36	-	-
	100	38	109	235	2.75	~ 0
	121	80 b)	85	180	49.0	0.11
	124	44	40	87	-	-
	300	63	19	60	-	-
	621	79	76	198	2.44	~ 0
	872	82	62	130	-	-
	1400	90	89	200	-	-
	2700	94	87	193	-	-
	6960	95	98	245	2.40	0.24
- 80	2850	12	39	89	-	-
	5580	28	60	120	-	-
	9870	34	246	586	-	-
	12985	31	203	466	-	-
	14000	56	307	709	-	-

a) $[2\text{-MOCB}]_0 = 1.68 \text{ mol} \cdot \ell^{-1}$
$[Et_3OPF_6]_0 = 2.7 \cdot 10^{-3} \text{ mol} \cdot \ell^{-1}$ in CH_2Cl_2

b) $[Et_3OPF_6]_0 = 5.85 \cdot 10^{-2} \text{ mol} \cdot \ell^{-1}$

c) Determined on the basis of the UV-absorbance at 372 nm after addition of NaOPh to the reaction mixture.

d) Determined on the basis of the UV-absorbance at 372 nm after removal of the phenetol originating from unreacted Et_3OPF_6.

This reaction would increase the proportion of polymer bound phenoxyl groups which result from the reaction with NaOPh. Although the above exchange reaction is not expected to be able to compete with the reaction between initiator and monomer its possible role should be further investigated perhaps also in case of polymerization of other cyclic ethers.

The failure of being able to determine the concentration of propagating oxonium ions during the early stages of the polymerization, where the kinetics should be studied, may be due to either a low rate of initiation or to termination which result in a reduction of the concentration of active species.

Gaschromatographic analysis of the products from the reaction with NaOPh confirmed that only a very small part of the triethyloxonium ions have been consumed in the initiation reaction even after a considerable time period since the amount of phenetole determined by the analysis is only a little less than that corresponding to the amount of charged initiator. It appears that growth of only relatively few chains is initiated but since the propagation is fast compared to termination good yields of polymers with very high molecular weight are obtained.

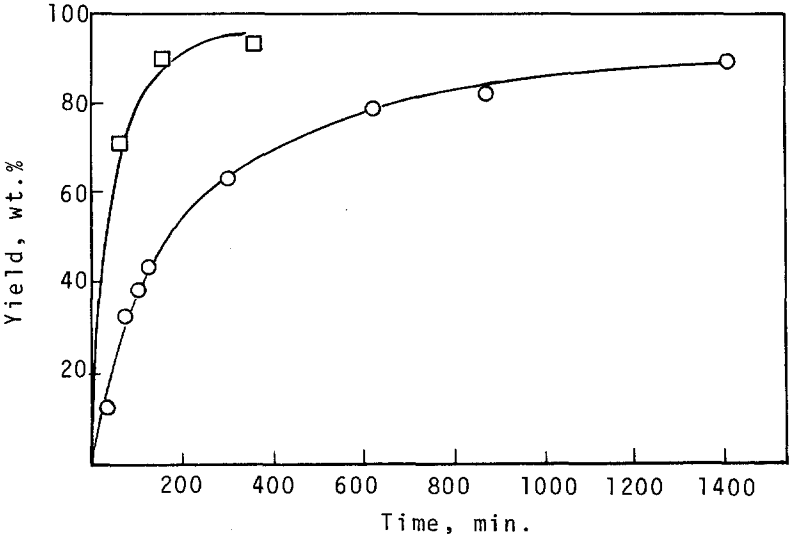


Fig. 1: Rate of conversion of 2-MOCB at-50°C (○) and -30°C (□).

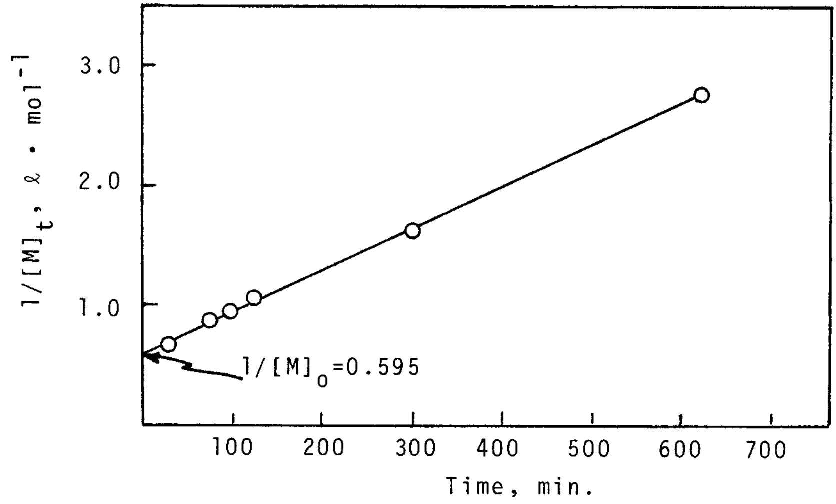


Fig. 2: Second order rate plot for 2-MOCB at -50°C.

In Figure 1 the rate of conversion is illustrated at two temperatures. In Figure 2 is shown a rate plot which conforms very well to a propagation which is second order in monomer. On this basis the following scheme is formulated:

$$R_i = k_i[I][M]$$
$$R_t = k_t[P^+]$$
$$R_p = k_p[M][P^+] = \frac{k_p k_i [I][M]^2}{k_t}$$

Upon integration:

$$\frac{1}{[M]} = \frac{k_p k_i [I]}{k_t} \cdot t + \frac{1}{[M]_o}$$

The straight line plot in Figure 2 is in accordance with the above equation and the initiator concentration is essentially constant during the early stages of the polymerization as already verified experimentally. In the scheme shown, the termination is spontaneous without the participation of monomer. However, other schemes could of course lead to the second order dependence on monomer, for example a higher order dependence on monomer in either the initiation reaction or in the propagation reaction although these latter possibilities appear less likely in the light of the current general knowledge about this type of polymerization.

Very high molecular weight polymers are obtained compared to previously and we attribute this to the particular care taken in the purification of the monomer and the initiator (see Experimental Section). The molecular weight values indicated in Table 1 should actually be even higher due to the fact that for most of the samples the molecular weight of a seizable part of the polymer is above the exclusion limit for the GPC columns. The molecular weights are somewhat erratic and it appears that the values are rather sensitive to small changes in the conditions. None of the polymers contained significant amounts of oligomers.

TABLE 2

Effect of changing conditions in the polymerization of 2-MOCB.

					GPC	
Temp. °C	React. time min.	2-MOCB conc. mol·ℓ$^{-1}$	Et_3OPF_6 conc. mol·ℓ$^{-1}$ ·10^3	Yield of pol.. wt.%	$\bar{M}_n$ ·10^{-3}	$\bar{M}_w$ ·10^{-3}
-30→0	150→6780	1.68	2.6	99	9	55
-30	151	1.68	2.7	90	22	84
0	90	1.68	2.6	86	7	25

The effect of temperature on conversion and molecular weight with respect to reversability of the polymerizations was studied and the data are presented in Table 2. It is seen that complete conversion is approached by carrying out the polymerization at 0°C and no reversability is observed up to that temperature. Furthermore, molecular weight changes are observed by changing the polymerization temperature. By first maintaining the temperature of -30°C for 150 minutes and then increasing the temperature and finishing the polymerization at 0°C a decrease in the molecular weight values is found in comparison with the experiments carried out at -30°C. The changes in the GPC curves show clearly a disappearence of the very highest molecular weight fraction upon changing the temperature. Thus a transfer to polymer is indicated which lead to degradation. A mechanism similar to that indicated in Equation (1) may be operating and degradation occurs when the polymeric oxonium ion is attacked by monomer. By comparison with the results of polymerization of 0°C it is seen that the system initially maintained at -30°C does not degrade to an extent where the molecular weight becomes comparable to the value for polymer obtained directly at 0°C at least not during the indicated time span.

The polymers prepared at the different temperatures were analyzed by ^{13}C NMR for head-to-head, tail-to-tail irregularities according to the previously described technique (KOPS et al., 1980b). A very good correspondance was found between the abundance of the various types of carbons in the different chain configurations. As required, the percentages of carbons appearing in head-to-head configurations were very close to those appearing in tail-to-tail configurations. The head-to-tail configurations increase with lower polymerization temperature, however, a high percentage (20-25%) of irregularities is produced even under those conditions. In the present study the polymerizations are performed under well controlled conditions and with the use of the same initiator in CH_2Cl_2 solution. In this system the amount of irregularities is determined only by the polymerization temperature.

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