

Non-equilibrium molecular weight studies on the metathesis polymerization of cyclopentene initiated by $WCl_6/Al i Bu_3$: Effect of catalyst ageing time

Allan J. Amass* and Jon A. Zurimendi†

Department of Chemistry, University of Aston, Gosta Green, Birmingham, B4 7ET, UK
(Received 8 April 1981)

A study has been made of the molecular weight and distribution changes that take place during the polymerization of cyclopentene initiated by the non-living metathesis catalyst $WCl_6/Al i Bu_3$. The system appears to be characterized by two distinct phases. In the first phase, the molecular weight distribution, which is bimodal, would appear to be kinetically controlled and the bimodal distribution to result from the presence of two kinetically independent metathesis species. The initial molecular weight distribution would, therefore, appear to be dependent upon the relative concentrations of these active species. The second phase of the polymerization is a slow conversion of the molecular weight distribution to that of an equilibrium distribution after a long reaction time.

Keywords Polymerization; catalysis; cyclopentene; molecular weight; ageing; kinetics

INTRODUCTION

Several authors¹⁻⁶ have shown that the ring-opening metathesis polymerization of cyclic alkenes produces polymers which have been shown by gel permeation chromatography to possess bimodal molecular weight distributions. It has also been shown that the molecular weight distribution may change during the course of conversion of monomer to polymer. The existence of ring-chain equilibria during the course of conversion has been established and there is undoubtedly evidence that the oligomeric material is cyclic. The final distribution of products in a catalytically active system may be described by the Stockmayer equation.

Several publications⁷⁻¹⁰ from these laboratories, however, have shown that the catalyst system $WCl_6/Al i Bu_3$ should not be considered to be a living system and furthermore that there may be more than one catalytically active species present in the polymerization. The composition of the catalyst system depends on the ageing time, which has been previously defined as the time elapsing between the additions of WCl_6 and $Al i Bu_3$ to the solution of cyclopentene. The present work was designed to study the effects of catalyst ageing time on the molecular weight distribution of the polymer and to compare these results with those published previously concerning the kinetics of the polymerization.

EXPERIMENTAL

Materials

Cyclopentene (CP), toluene and tungsten hexachloride were purified by the techniques described previously, and solutions of WCl_6 and $Al i Bu_3$ were prepared and stored in the containers described in ref. 8. A stock solution of cyclopentene in toluene was prepared for this series of

experiments so that the polymerizations could be studied under conditions of constant initial monomer concentration.

Polymerization and sample preparation

The apparatus shown in *Figure 1* was used to polymerize cyclopentene and extract samples of polymer at various stages during the course of the polymerization. The reaction vessel was connected to the stock solution container by way of the greaseless joint A, and the whole apparatus was evacuated. Tap D was closed and the required amount of monomer solution was allowed to pour into the reaction vessel. When tap C was closed, WCl_6 solution was injected through the rubber septum E followed, after a pre-determined time, by the $Al i Bu_3$ solution.

Samples could be taken at different stages of the reaction. The collecting flask (G) when connected to the inverted reaction flask (F) by way of the greaseless joints (B) and (K) was evacuated through (H) and (J). When a high vacuum was obtained, tap (H) was closed and the whole apparatus was removed from the vacuum line. A sample of solution was taken through tap (D) and the apparatus separated. In order to quench the reaction, wet chloroform was introduced. The solvent and remaining monomer were steam distilled; the polymer sample was

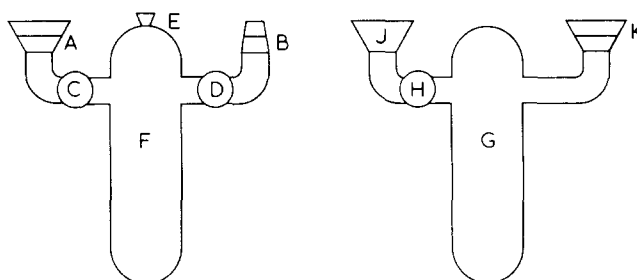


Figure 1 Apparatus used for preparation of polymer samples

* To whom all correspondence should be sent

† Present address: Department of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT

then dried under vacuum and stored in sealed ampoules in the refrigerator until solutions were prepared.

Analysis

Analysis of the polymer samples was carried out by gel permeation chromatography (g.p.c.) using a Waters 6000 fitted with 4 μ Styragel columns with exclusion limits of 10^2 , 10^3 , 10^4 and 10^5 Å; a differential refractometer was used as detector.

RESULTS

Figure 2 shows the gel permeation chromatograph of a sample of polymer produced in these studies and is typical of those obtained. The chromatogram shows two different peaks, one corresponding to high molecular weight polymer (exclusion volume 18 to 26 ml) and the other corresponding to low molecular weight oligomers (exclusion volume 36 to 41 ml).

The chromatography columns were calibrated using characterized samples of polystyrene and hence it was possible to determine readily the polystyrene equivalent gel permeation number average and weight average

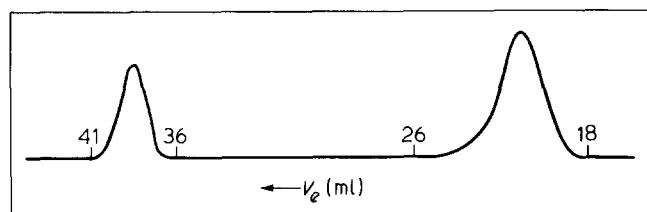


Figure 2 Typical gel permeation chromatograph

molecular weights of the polymers, particularly for the higher molecular weight portions. Such simple analyses were not possible for the lower molecular weight portion of the chromatogram since in this region, it is likely that the differential refractive indices were dependent upon the molecular weights of the oligomers. Although no absolute interpretation of results was possible, the ratio of the areas under the high and low molecular weight peaks was considered to be an indication of the comparative amounts of the respective materials present in the sample.

Table 1 shows the results obtained for this series of studies. A series of polymerizations was carried out in which the ageing time of WCl_6 with CP was varied from 1 to 15 min. For each polymerization a number of samples were taken at various reaction times from 2 min to 24 or 72 h. The results shown in Table 1, if not conclusive, point to the general behaviour of the system:

(i) Within experimental error, the number average molecular weight of the high molecular weight fraction decreases with conversion and the molecular weight distribution broadens.

(ii) The ratio of the areas under the high to the low molecular weight peaks decreases initially and subsequently increases at high conversions and/or reaction times for all ageing times.

(iii) Comparison of the ratios of the areas under the peaks of a common polymerization time (e.g. 20 min) indicates that this ratio depends on the ageing time of the initiator as shown in Figure 3. Although the figures are not available, a similar marked dependence can be seen to occur in the earlier stages of the reaction.

(iv) The ratio of the areas are practically identical after long polymerization times for all ageing times.

Table 1 Dependence of molecular weight and distribution on ageing time and conversion

Ageing time (min)	Reaction time (min)	High mol. wt. fraction			Fraction area of high to low mol. wt. peaks
		Equivalent $\bar{M}_n \times 10^{-5}$	Equivalent $\bar{M}_w \times 10^{-5}$	\bar{M}_w/\bar{M}_n	
1	2	7.8	16.7	2.1	6.9
	6	5.6	13.9	2.5	2.4
	20	5.5	12.8	2.4	1.4
	50	4.3	10.7	2.5	2.1
	24 x 60	4.0	10.4	2.7	3.7
2	1.5	4.5	11.0	2.5	10.1
	20	5.3	12.9	2.5	2.3
	50	5.9	14.0	3.4	2.0
	200	4.6	12.4	2.8	3.2
	72 x 60	3.3	9.0	2.8	3.7
3	3	6.1	14.6	2.4	4.5
	10	4.7	11.0	2.4	2.1
	20	5.0	12.0	2.4	2.0
	50	4.1	10.2	2.5	2.0
	24 x 60	3.7	9.4	2.6	3.4
5	4	7.5	16.4	2.2	4.5
	20	4.4	11.3	2.5	1.6
	50	5.0	12.1	2.4	1.5
	24 x 60	3.7	8.9	2.4	3.7
15	10	6.1	13.9	2.3	2.4
	20	4.9	11.9	2.4	1.9
	50	4.0	9.7	2.4	1.6
	24 x 60	2.9	7.3	2.5	3.8

([CP] 2.6, $[WCl_6] = 1.04 \times 10^{-3}$, $[Al(iBu)_3] = 2.08 \times 10^{-3}$ mol dm $^{-3}$; temperature = 25°C)

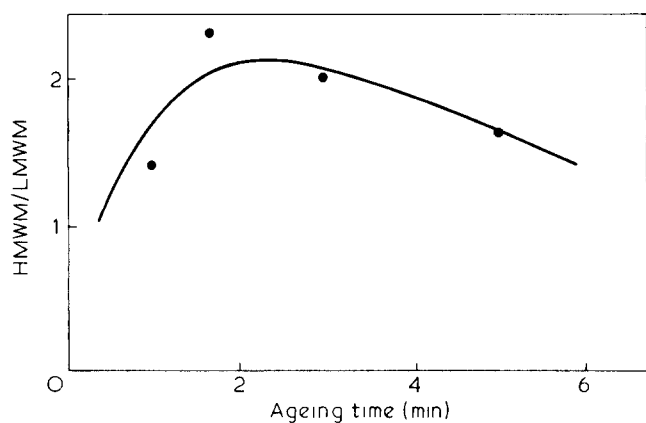


Figure 3 Dependence of composition of polymer on ageing time of catalyst

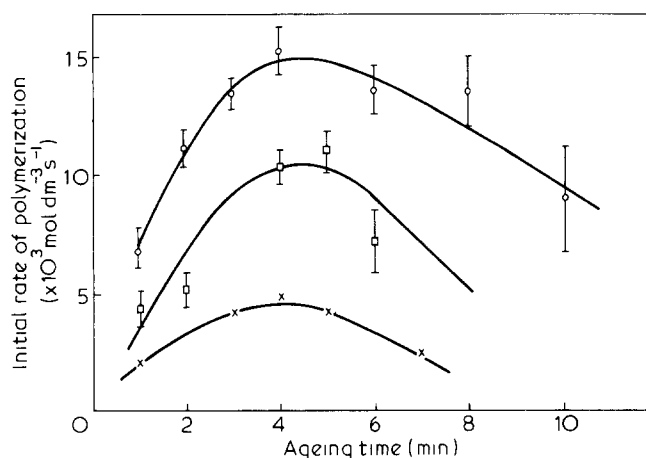
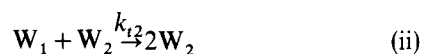
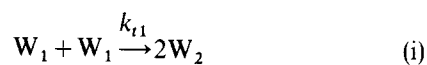


Figure 4 Dependence of initial rate of polymerization, determined by dilatometry, on catalyst ageing time. $[CP] = 1.75 \text{ mol dm}^{-3}$, $[WCl_6]$ (O) = 8×10^{-4} ; (□) = 5×10^{-4} ; (X) = $2.5 \times 10^{-3} \text{ mol dm}^{-3}$

DISCUSSION AND CONCLUSIONS

A plot of the ratio of the areas under the high and low molecular weight peaks as a function of time would show that, for each ageing time, there is initially a decrease, then an increase in the ratio to an almost constant value. It would appear, therefore, that there may be two distinct phases to the polymerization under study, the initial stage which would be kinetically controlled and the later stage which would be thermodynamically controlled, eventually leading the system to equilibrium.

A recent publication discussed the kinetic nature of the particular system under study⁹. Undoubtedly the $WCl_6/AliBu_3$ catalysed polymerization of cyclopentene is not a living system. An important feature of the kinetic chain mechanism proposed for the polymerization is the occurrence of termination reactions. The termination reactions are second order and a kinetic scheme that accounted for the deceleration of the dilatometrically determined rate of polymerization was proposed as follows:



where W_1 is the propagating centre producing high molecular weight polymer and W_2 is the species produced on termination, the role of which will be discussed shortly. If the polymerization were considered as a simple second order termination reaction, the number average degree of polymerization (\bar{x}_n) would be given by:

$$\bar{x}_n = \frac{k_p[CP]}{2k_{t1}[W_1]}$$

Analysis of the kinetic curves shows that in many cases, the concentration of active species decreases at a rate greater than that of the monomer and hence $[CP]/[W_{act}]$ would increase. It would appear therefore that the observed small decrease in \bar{M}_n can only be explained if the second termination reaction, the rate of which will increase with conversion, is included, such that there is a progressive change in the kinetic nature of the system. Then:

$$\bar{x}_n = \frac{k_p[CP]}{2k_{t1}[W_1] + k_{t2}[W_2]}$$

This explanation is in line with other conclusions drawn in previous publications^{9,10}.

Figure 3 shows the dependence on ageing time of the ratio of the areas under the chromatograph for high to low molecular weight material. The shape of the curve is similar to those obtained by dilatometry (Figure 4) and calorimetry (Figure 5), for the dependence of the initial rate of polymerization and rate of monomer consumption on ageing time respectively^{7,8}. All curves show a maximum at the same ageing time suggesting a common explanation for the phenomenon.

The shapes of the curves could be explained by the presence of more than one active species in the system, one capable of producing high molecular weight material (HMWM) and the other(s) capable of producing low molecular weight material (LMWM). The initial concentration of the species capable of producing HMWM could depend on ageing time in a manner similar to that suggested by Amass and Tuck⁷. In this respect, the species W_1 would be that which produced HMWM, but the role of W_2 at the present is uncertain. It is possible that W_2 , although inactive towards the production of HMWM, may lead to the LMWM seen in the gel permeation chromatogram. In this way, the ageing time at which the maximum initial rate of polymerization is obtained (t_{max}) would be that at which the ratio of the

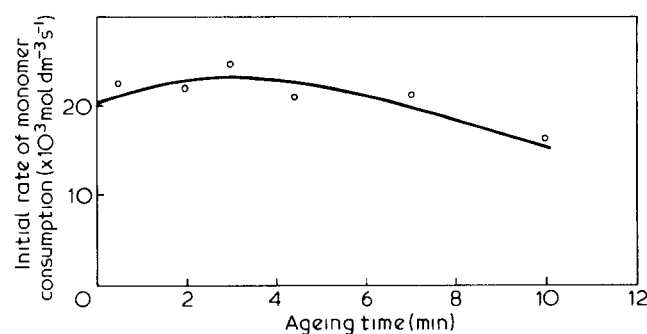


Figure 5 Dependence of rate of consumption of monomer, determined calorimetrically on catalyst ageing time

catalyst capable of producing HMWM to the catalyst capable of producing LMWM is a maximum.

Comparison of the appropriate values for the ratio of areas under the high with low molecular weight peaks indicate that the maximum corresponds to an ageing time that would give a maximum dilatometric rate of polymerization. It is therefore suggested that during the early stages of the polymerization, the molecular weight distribution is kinetically controlled.

A comparison of the final compositions of each polymer suggests that even in this system the polymerization reaches a thermodynamic equilibrium irrespective of the nature of the initiating system. A publication to be presented shortly shows that molecular oxygen has an activating effect upon terminated polymerization systems and so it is quite possible that slight leakages have resulted in the regeneration of the activity of the catalyst. The equilibrium conditions are

then probably those already described by Höcker⁵ and Chauvin⁶.

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