This article was downloaded by: On: *25 January 2011* Access details: *Access Details: Free Access* Publisher *Taylor & Francis* Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713597274

Penultimate Unit influence in the Cationic Copolymerization of Tetrahydrofuran with Oxetanes

Przemysław Kubisa^a; Stanisław Penczek^a ^a Center of Molecular and Macromolecular Studies Polish Academy of Sciences, Lódz 40, Poland

To cite this Article Kubisa, Przemyslaw and Penczek, Stanislaw(1973) 'Penultimate Unit influence in the Cationic Copolymerization of Tetrahydrofuran with Oxetanes', Journal of Macromolecular Science, Part A, 7: 7, 1509 — 1524 To link to this Article: DOI: 10.1080/10601327308060516 URL: http://dx.doi.org/10.1080/10601327308060516

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Penultimate Unit Influence in the Cationic Copolymerization of Tetrahydrofuran with Oxetanes

PRZEMYSŁAW KUBISA and STANISŁAW PENCZEK

Center of Molecular and Macromolecular Studies Polish Academy of Sciences Łódź 40, Poland

ABSTRACT

Copolymerization of exetanes (OX) with tetrahydrofuran (THF) above the ceiling temperature of THF leads to the formation of highly ordered copolymers if a large excess of THF (M_2) is used. At [THF]/[OX] - ∞ in the monomer feed, the alternating copolymer with a limiting composition [thf]/[ox] - 1:1 results if OX is 3,3-dimethyloxetane (DMO) or 3,3-bis(fluoromethyl)oxetane (BFMO). In a copolymerization with 3,3-bis(chloromethyl)oxetane (BCMO) the limiting copolymer composition is close to 2:1.

These data suggest the influence of the penultimate unit in the latter pair due to the presence of the bulky chloromethyl groups. This influence is of electronic rather than of steric character since no difference in the structure of copolymers was observed for DMO and BFMO.

Analysis of the Stuart molecular models reveals that the chloromethyl groups of BCMO adjacent to the growing center, $+ bcmo + \frac{1}{0}$, are frozen and cannot rotate freely. Thus the depropagation step of a $\sim m_1 m_2 m_2^*$ sequence, involving the

1509

Copyright © 1973 by Marcel Dekker, Inc. All Rights Reserved. Neither this work nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

back bending within + bcmo + thf + o

with a much more negative entropy of activation than the depropagation step of the similar sequence involving DMO or BFMO. Therefore the depropagation of the former is slower than that of the latter.

The simplified kinetic scheme, applied for a copolymerization above the T_c of THF, allowed the reactivity ratios

to be determined.

Reversibility is a common but seldom acknowledged feature in the ionic copolymerization of heterocyclic monomers. Depropagation of one or both of the comonomers influences both the copolymerization kinetics and resulting copolymer structure. Particularly pronounced effects are observed in copolymerization above the ceiling temperature $(T_{r_{e}})$ of at least one of the comonomers [1].

The influence of depropagation in the copolymerization of tetrahydrofuran (THF) was observed by one of us previously [2]. The application of the Lowry's general treatment of the reversible copolymerizations for the THF-BCMO [3,3-bis(chloromethyl)oxetane] pair below T_{c} of THF was described by Yamashita et al. [3].

In the present work the copolymerization of THF with three different oxetanes above the T_c of THF was studied:



The dependence of the ultimate copolymer composition (at [THF]. $[OX] - \infty$) on the oxetane (OX) structure is described and the reactivity ratios were determined.

EXPERIMENTAL

All the copolymerizations were conducted in sealed ampoules, in bulk, with Al $(i-Bu)_3$ as catalyst [2]. Special care was paid to stop copolymerization conducted above T_c at the temperature of the

TETRAHYDROFURAN WITH OXETANES

experiment. Ampoules were filled in a stream of prepurified N_2 or on a high-vacuum manifold.

THF was purified according to a known procedure -[4] and was finally distilled from a violet Na-benzophenone complex just before use.

DMO was prepared by the direct addition of a neopentylglycol solution in H_2SO_4 to a boiling NaOH solution, according to Shmoyer [5]. BCMO was prepared and purified as earlier described by one of us [6], and BFMO was prepared directly from BCMO by using anhydrous KF in boiling ethylene glycol [7].

All of the copolymerizations were stopped at low conversions, not exceeding 5-7%, by fast cooling in liquid nitrogen, followed by addition of water solution in THF. Copolymers were isolated and freed from monomer by heating the monomer-polymer mixture in boiling water until no more monomer was evolved. Independent measurements, using the GLC technique, proved this method to be effective. Compositions of the obtained copolymers were determined by elemental analysis, and in some cases checked by IR and NMR.

RESULTS AND DISCUSSION

Composition of Copolymers

The experimentally observed dependence of $m_2/(m_1 + m_2)$ on $[M_2]/([M_1] + [M_2])$ (m_2 and M_2 always refer to THF polymer and monomer, respectively) are shown in Figs. 1, 2, and 3 in copolymerizations at 30 and 120° with DMO, BFMO, and BCMO, respectively. It follows from an examination of the data obtained above the T_c

of THF (at 120°) that the DMO-THF and BFMO-THF pairs give the 1:1 limiting compositions (at ([THF]/[M_1]) - ∞).

In the copolymerization of BCMO with THF the limiting composition is closer to $[(bcmo) (-thf)_2]_n$ (67% of THF units) than to $[(+bcmo) (-(thf)_3]_n$ (75% of THF units). Exact determination of the limiting structure is difficult because of some scatter in the experimental data. This behavior of the BCMO-THF pair, allowing the limiting structure $[(+bcmo) + (thf) + 2]_n$ to be formed above the T_c of THF, has been noted by one of us previously [2] and interpreted in terms of penultimate unit influence.

Thus a question should be asked: Why is the penultimate unit influence observed in the BCMO-THF copolymerization while in both DMO-THF and BFMO-THF pairs there is no influence of this kind. To answer this question, the mechanism of chain growth and depolymerization should first be considered.



FIG. 1. Dependence of copolymer composition on monomer feed in copolymerization of DMO with THF at 30 and 120° .

According to current views [8], the active species in the polymerizations of both THF and oxetanes have the structure of tertiary oxonium ions:



where $R = CH_3$, CH_2F , or CH_2Cl in this paper.

This structure has several important consequences in the copolymerization itself, since every depolymerization step should be assisted by a cyclization of the penultimate unit [9], e.g.,



FIG. 2. Dependence of copolymer composition on monomer feed in copolymerization of BFMO with THF at 30 and 120°.



FIG. 3. Dependence of copolymer composition on monomer feed in copolymerization of BCMO with THF at 30 and 120° .

Thus, before a monomer molecule splits off the chain end, a partial bond within a penultimate unit is formed in the transition state. If the antepenultimate unit in the depropagation step, underlined by a wavy line in the formulas above, is similar in structure to the last two units, then no additional interactions should be taken into account. Therefore there is no reason to expect that above $T_c(THF)$ a sequence

of two or more THF units can be introduced into a copolymer chain. These conditions are met in the copolymerization of DMO and BFMO with THF. Apparently the presence of $-CH_1$ and $-CH_2F$ groups (encircled in the schemes below) does not disturb the properties of the active centers bearing THF molecules at their ends:

For this reason the equilibrium constants of the polymerizationdepolymerization equilibrium are identical for THF for both



homopolymer and copolymer, involving DMO or BFMO. Obviously, at limiting conditions ($[THF]/[M_1] - \infty$) the copolymer structure tends toward an alternating $[+thf] + (m_1 + m_1)_n$ structure.

The experimental data show that in the copolymerization of the BCMO-THF pair the influence of the penultimate unit structure (or in antepenultimate in the depropagation step) cannot be neglected. Among the possible structures of the active centers bearing a THF unit at their ends:

+ bcmo ++ bcmo +
$$\dot{0}$$
, + bcmo ++ thf + \dot{c} , and + thf ++ \dot{t} f = II

only I and II are able to depropagate (inability of the $-bcmo-\delta$ unit to depropagate is discussed in the next section). The equilibrium constant (K₂) of the propagation-depropagation-equilibrium in II is similar to that for homopropagation, since there is no experimental evidence indicating any influence of more remote units (e.g., an antepenultimate unit in chain growth, leading, after THF molecule addition, to the structure +bcmo ++thf ++thf + 0).

The equilibrium constant K_1 in I should, however, be larger than K_2 in II and in homopropagation if a limiting composition $[+bcmo+(+thf)+_2]_n$ is to be observed.

 K_1 and K_2 are defined as $K_1 > 0$, $K_2 = 0$ [above T_c (THF)], and,

+ bcmo +
$$0$$
 + 0 $\frac{k_{22}}{k_{-22}}$ + bcmo ++ thf + 0 ; $K_1 = k_{22}/k_{-22}$
I

+
$$\ln f + 0$$
 + 0 $\frac{k_{222}}{k_{-222}}$ + $\ln f + \ln f + 0$; $K_2 = k_{222}/k_{-222}$
II

therefore, $T_c' > T_c$, where T_c' corresponds to the ceiling temperature of THF addition to the active center +bcmo + o. Obviously, at this temperature $K_1 = 0$.

At the copolymerization temperature equal to, e.g., T_c (THF) and related to the equilibrium involving the active center II, the equilibrium monomer concentration with that active center is $[M_2]_{eII}$ =

 k_{-222}/k_{222} and is higher than $[M_2]_{eI} = k_{-22}/k_{22}$. Remembering that ln $[M_2]_e = -\ln K_e = \Delta H_p/RT - \Delta S_p/R$, the influence of the penultimate unit will be apparent if it leads to an increase in the exothermicity of polymerization (more negative ΔH_p) or to an increase in the entropy of THF addition to the influenced active center (here I) in comparison with a homopropagation (addition to the center II).

If we, therefore, denote $\Delta H_{pI} - \Delta H_{pII} = \Delta \Delta H_p$ and $\Delta S_{pI} - \Delta S_{pII} = \Delta \Delta S_p$, then, to fulfill the requirement $K_1 > K_2$, $\ln K_{eII} - \ln K_{eII} > 0$, and, therefore,

$$(-\Delta H_{pI} + \Delta H_{pII})/RT + (\Delta S_{pI} - \Delta S_{pII})/R > 0$$
(1)

OF

$$\Delta \Delta H_{p} - T \Delta \Delta S_{p} > 0 \tag{1a}$$

Therefore the enrichment of a copolymer with the depropagating comonomer will proceed independently of the copolymerization temperature, if simultaneously $\Delta\Delta H_p < 0$ and $\Delta\Delta S_p > 0$. If, however, simultaneously $\Delta\Delta H_p > 0$ and $\Delta\Delta S_p < 0$, then no enrichment could be observed. The two other remaining cases are temperature-dependent. Both ΔH_p and ΔS_p are equal to the differences in the corresponding

activation parameters in the depolymerization and propagation processes, e.g., $\Delta H_p = \Delta H_p^* - \Delta H_d^*$, and the influence of the penultimate unit structure on the equilibrium constant K_e should be discussed in terms of these parameters.

The possibility of a direct electronic effect, which could account for the observed inequality $K_1 > K_2$, is ruled out since no penultimate unit effect was observed in the copolymerization of THF with BFMO. Thus only an electronic space effect or steric effect, both a consequence of the large size of the chloromethyl group, can operate.

The net effect of an electronic interaction of $-CH_2Cl$ groups with an active center is a lowering of its electrophilicity due to the electronwithdrawing effect at the Cl-atoms. Thus the formation of an activated complex in the propagation step is more difficult because less energy is released in the interaction of the lone electron pair of the incoming

TETRAHYDROFURAN WITH OXETANES

monomer molecule with an active center. In depolymerization the last unit is attached by a sigma bond, and due to the above-mentioned interaction, the enthalpy of activation in depolymerization $(\Delta H_{\rm eff}^{+})$ is

influenced by two counteracting effects. Bond breaking, leading to the release of the last unit, is facilitated (in comparison with II); bond making, however, within the new last unit is hindered for the same reason. It is difficult to decide which of these effects outweighs the other and, therefore, whether $\Delta \Delta H_{\rm p}$ is positive or negative.

The presence of two bulky chloromethyl groups close to the active center should also influence entropies of activation in both the chain growth and depropagation. Again, when compared with homopropagation (structure II), the simple steric effect makes the entropy of activation more negative, thus $\Delta S_{pI}^{\dagger} < \Delta S_{pII}^{\dagger}$. In depolymerization, however, for the same reason, $\Delta S_{dI}^{\dagger} < \Delta S_{dII}^{\dagger}$, and it is difficult to decide about the actual sign of $\Delta \Delta S_{p}$.

Analysis of the molecular models has, however, revealed that the reverse influence of the proximity of the active center on the mobility of the chloromethyl groups should also be considered.

Indeed, in $+bcmo + \delta$, both chloromethyl groups are frozen.

On the other hand, in + bcmo ++ thf + $\frac{1}{\sqrt{2}}$, formed after addition of

a THF molecule to the already discussed active center, both $-CH_2Cl$ groups in a +bcmo mer rotate freely. When, however, the two last units bend back to form an activated complex for a depropagation step, the chloromethyl groups become frozen again. For this reason the activation entropy of depropagation is more negative for this active center and the depropagation reaction becomes less probable than depropagation involving IL

This is sufficient to make $\Delta S_{pI} > \Delta S_{p\Pi}$ (it should be remembered, that $\Delta S_p = \Delta S_p^* - \Delta S_d^*$) and, eventually, $K_1 > K_2$.

Therefore the immobilization of the chloromethyl groups, adjacent to the active center and bearing a THF molecule at its end, is responsible for the observed penultimate effect, manifested in the formation of the copolymer of the structure $\frac{\int (bcmo) (thf)_2}{2}$ above the ceiling temperature of THF and with a large excess of THF in the monomer feed.

Determination of the Copolymerization Parameters

In the previous paper of this series the following kinetic scheme was proposed to describe the copolymerization of THF with oxetanes:

$$\sim m_1^* + M_1 \xrightarrow{k_{11}} \sim m_1^*$$
 (2)

 $\sim m_1^* + M_2 \xrightarrow{k_{12}} \sim m_1 m_2^*$ (3)

$$\sim m_1 m_2^* + M_2 \frac{K_{22}}{K_{-22}} \sim m_2 m_2^*$$
 (4)

$$\sim m_1 m_2 m_2^* + M_2 \frac{k_{222}}{k_{-222}} \sim m_2 m_2 m_2^*$$
 (5)

$$\sim m_1(m_2)_n m_2^* + M_1 \longrightarrow \sim m_1(m_2)_{n+1} m_1^* n \ge 0$$
 (6)

This scheme was based on the following facts and assumptions:

Equation (2): The chain propagation of oxetanes is treated as a practically irreversible reaction because of the high ring-strain in the four-membered rings (e.g., ΔH_p in both oxetane and 3,3-dimethyl-oxetane is higher than 20 kcal/mole compared to only 5-6 kcal/mole for THF polymerization [8]).

Equation (3): Addition of the THF molecule to the active center bearing an oxetane monomer at its end is irreversible because the depropagation step would require the back cyclization of the fourmembered oxetane ring.

Equations (4) and (5): Addition of THF to its own active center is reversible. Since in the limited composition of the copolymer prepared above the T_c (THF) the number of -thf- units separated by

an $-\infty$ - unit does not exceed two, then the next equilibrium constant, namely $K_3 = k_{2222}/k_{-2222}$, should always be zero because $k_{-2222} \gg k_{22222}$. In all of the cases studied, $K_2 = 0$ for the same reason and $K_1 = K_2 = 0$ for both DMO and BFMO.

Equation (6): Addition of an oxetane to the active center bearing a THF molecule at its end is irreversible because, due to the high strain of the four-membered ring, the rate of the four-membered ring opening is higher than the rate of the five-membered ringclosing:



Some of the elements of the present scheme have been considered previously by Yamashita et al. (eq. III) [3].

The general solution of this scheme, with an assumption that $K_3 = 0$, was given by one of us previously [9] in the form of the composition equation:

$$\frac{m_1}{m_2} = \frac{(r_1 [M_1] + 1) (1 + \alpha + \beta)}{1 + 2\alpha + 3\beta}$$
(7)

where

$$\alpha = \frac{\left[\mathbf{m}_{1}\mathbf{m}_{2}\mathbf{m}_{2}^{*}\right]}{\left[\sim\mathbf{m}_{1}\mathbf{m}_{2}^{*}\right]} = \frac{\left[\mathbf{M}_{2}\right]}{\frac{1}{\mathbf{K}_{1}} + \frac{1}{\mathbf{r}_{2}}\left[\mathbf{M}_{1}\right] + \frac{\mathbf{K}_{2}^{2}\mathbf{r}_{2}\left[\mathbf{M}_{2}\right]}{\mathbf{r}_{2} + \mathbf{K}_{2}\left[\mathbf{M}_{1}\right]}}$$
(8)

$$\beta = \frac{\left[\sim m_1 m_2 m_2 m_2^{\dagger} \right]}{\left[\sim m_1 m_2 m_2^{\dagger} \right]} = \frac{\left[M_2 \right]}{\frac{1}{K_2} + \frac{1}{r_2} \left[M_1 \right]}$$
(9)

 $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, and K_1 and K_2 were both defined above. Since the limiting composition for the BCMO-THF pair does not include sequences $-(thf)_3$, it can be assumed that $\beta = 0$, and therefore $K_2 = 0$. In copolymerizations with DMO and BFMO the limiting composition is simply $-(\alpha x) - (thf)$, and therefore $\alpha = \beta = 0$ and K, and K₂ = 0. For these conditions Eq. (7) converts to its simplest form:

$$\frac{m_1}{m_2} = 1 + r_1 \frac{[M_1]}{[M_2]}$$
(10)

To find the required value of r_1 from the experimental data, m_1/m_2 is plotted against $[M_1]/[M_2]$. This is shown in Figs. 4 and 5 for DMO and BFMO, respectively.

Both sets of data were obtained at 120° , about 40° above the T_c (THF).

The linearity of the slopes and the intercepts equal to unity in the copolymerization of both pairs confirm the validity of Eq. (10).

From the slopes of the straight lines the r_1 values were measured; $r_1(DMO) = 4.5$, $r_1(BFMO) = 0.25$.

The dependence of m_1/m_2 on $[M_1]/[M_2]$ for the BCMO-THF pair,



FIG. 4. Determination of $r_1 = k_{11}/k_{12}$ in copolymerization of DMO (M_1) with THF (M_2) at 120°.



FIG. 5. Determination of r_1 in copolymerization of BFMO (M_1) with THF (M_2) at 120°.

measured at 120° (Fig. 6), is not, however, a straight line, and cannot be treated according to Eq. (10) for which $\alpha = \beta = 0$.

The limiting composition of BCMO-THF copolymer is close to 1:2 (cf. Fig. 3), therefore $\alpha \neq 0$ and $\beta = 0$. To determine the independent copolymerization parameters K_1, r_1 , and r_2, r_1 was first measured as the slope of the tangent to the experimental plot, relating m_1/m_2 and $[M_1]/[M_2]$ (Fig. 6), when $[M_2]/[M_1] \rightarrow 0$ ($\alpha \rightarrow 0$).

Thus from Fig. 6, $r_1(BCMO) = 0.35$. According to expectations, this value is very close to that obtained for the BFMO-THF pair (0.25). It should also be noted that the "intercept" in Fig. 6 is close to 1/2. According to Eq. (7), when $[M_1]/[M_2] = 0$, then $m_1/m_2 = 1/2$.

To determine both K_1 and r_2 , a knowledge of the dependence of α on $[M_1]/[M_2]$ is required. By rearranging Eq. (7) ($\beta = 0$), one obtains α as a function of $[M_1]/[M_2]$ and m_1/m_2 :

$$\alpha = \frac{(m_1/m_2) - r_1[M_1]/[M_2] - 1}{2(m_1/m_2) - r_1[M_1]/[M_2] - 1}$$
(11)



FIG. 6. Determination of r_1 and $\alpha = \{m_1 m_2 m_2^*\} / \{m_1 m_2^*\}$ in copolymerization of BCMO with THF at 120°.

Since $[M_1]/[M_2]$ and m_1/m_2 are interdependent, the corresponding values can be taken from the plot of Fig. 6 and then the related α 's are easily calculated from Eq. (11). These values are given in Table 1.

TABLE 1. Numerical Values of α Determined from the Plot in Fig. 6 According to Eq. (11) (r_1 (BCMO) = 6.35)

[M ₁]/[M ₂]	0.1	0.5	2.0	5, 0	10.0
m_1/m_2	0.55	0.65	1.0	1.9	3.2
$\alpha = \frac{\{ \mathbf{m}_{1} \mathbf{m}_{2} \mathbf{m}_{2}^{*} \}}{\{ \mathbf{m}_{1} \mathbf{m}_{2}^{*} \}}$	7.5	4.0	2.3	0.81	0.69



FIG. 7. Dependence of $[M_2]/\alpha$ on $[M_1]$ and determination of K_1 and r_2 in copolymerization of BCMO with THF at 120°.

By rearranging Eq. (7) in which $K_2 = 0$, we get an equation from which both K_1 and r_2 can independently be determined:

[M ₂]		1	[M ₁]	
	ŧ		+	(12)
α		K,	[r ₂]	

By plotting the left-hand side of this equation against $[M_1]$, K_1 is obtained from an intercept and r_2 from a slope. This dependence is plotted (BCMO + THF at 120°) in Fig. 7. Thus $K_1 = 0.8$ mole/liter and $r_2 = 9.0$.

If we now compare the determined reactivity ratios with the corresponding pK_b values, recalling the basicities of the monomers involved, a good correlation is observed. Thus pK_b values are oxetane = 3.13 (DMO should be close to it), BCMO = 5.65, and THF = 5.00; the corresponding r values are r_1 (DMO) = 4.5, r_1 (BCMO) = 0.35, r_1 (BFMO) = 0.25, and r_2 (THF) (in copolymerization with BCMO) = 9.0.

REFERENCES

- G. G. Lowry, J. Polym. Sci., 62, 463 (1960). [1]
- 2 L Penczek and S. Penczek, Ibid., B, 5, 367 (1967).
- [3] Y. Yamashita, H. Kasahara, K. Suyama, and M. Okada, Makromol. Chem., 117, 242 (1968).
- [4] M. Szwarc, Carbanions, Living Polymer and Electron Transfer Processes, Interscience, New York, 1968.
- r 51 L. F. Schmoyer and L. O. Case, Nature, 187, 592 (1962).
- 6 M. Legocki, M. Markowicz, L Penczek, and S. Penczek, J. Prakt. Chem. USSR 34, 640 (1961).
- [7] Y. Etienne, Ind. Plast. Mod., 9(6), 37 (1957).
 [8] P. Dreyfuss and M. P. Dreyfuss, "1,3-Epoxides and Higher Epoxides," in Ring Opening Polymerization (K. C. Frisch and S. L. Reegen ed.), Dekker, New York, 1969.
- [9] S. Penczek, Bull. Acad. Pol. Sci., Ser. Sci. Chim., In Press.