Polymer Bulletin 47, 485-492 (2002)

Polymer Bulletin

Study of the cationic photopolymerization kinetics of cyclic acetals

Magdalena Pantiru [1, 4] (✉), **Dumitru Mircea Vuluga** [2], **Dan Sorin Vasilescu** [3], **Marc J. M. Abadie** [4]

[1]Institute of Chemical Research - ICECHIM, 202 Splaiul Independentei, CP 15-159, 77208-Bucharest, Romania
[2]Romanian Academy, Center for Organic Chemistry “C.D.Nenitescu”, 202B Splaiul Independentei, CP 15-258, 76250-Bucharest, Romania
[3]“POLITEHNICA” University of Bucharest, Laboratory of Macromolecular Compounds, 149 Calea Victoriei, 71101-Bucharest, Romania
[4]Université Montpellier 2 - LEMP/MAO, Case courrier 21, 34095-Montpellier, France
e-mail: pantiru@lcpp.cpe.fr, Fax: + 334 72 43 17 68

Received: 19 July 2000/Revised version: 8 November 2001/ Accepted: 8 November 2001

Summary

Photocationic polymerization for three cyclic acetals, namely 1,3-dioxolane, 1,3-dioxepane and 1,3,6-trioxocane, respectively, has been studied. Several cationic photo-initiators (diaryliodonium or triarylsulfonium salts, and one arene-metal complex) have been used. Differential scanning photo-calorimetry (DPC) has been employed to record the dependence conversion versus time. DPC thermogrames, in turn, have been utilized to calculate the propagation reaction constants as well as the corresponding activation energies. The values for the propagation constants at 30°C are $1.6 \cdot 10^2$ L/mol·s for 1,3-dioxolane, using a diaryliodonium salt as photoinitiator, $1.6 \cdot 10^3$ L/mol·s for 1,3-dioxepane and $6.1 \cdot 10^3$ L/mol·s for 1,3,6-trioxocane, respectively, in the presence of a triarylsulfonium salt as photoinitiator. The activation energies are in the range of 9.6÷19.6 kcal/mole.

Introduction

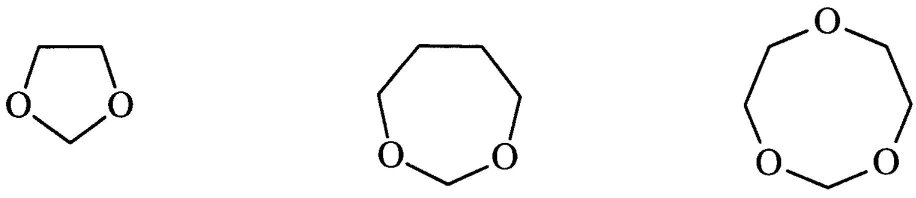
Cyclic acetals may be polymerized by Brönsted as well as by Lewis acids [1], by several silicon compounds [2] or by photochemical means [3]. Propagation is reversible and various active sites may be existing. Moreover, chain transfer (inter- or intramolecular) makes the cationic polymerization of cyclic acetals a very complex process [4].

The obvious advantages introduced by photoinitiated polymerization (short time reaction, low energy required) made it possible to extend this procedure for cyclic acetals; evidently, the process keeps its cationic nature [5-7].

Experimental

Materials

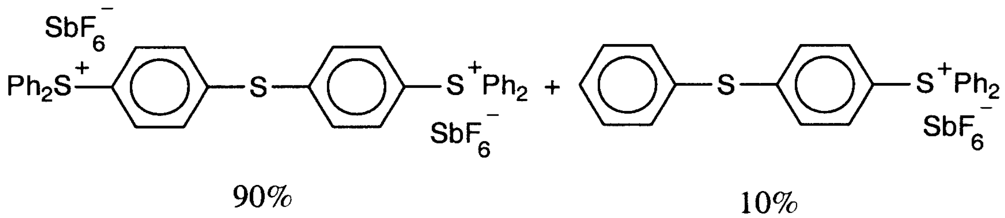
The cyclic acetals (figure 1), 1,3-dioxolane (DXL), 1,3-dioxepane (DH) and 1,3,6-trioxocane (TOC), were prepared by Astle's method [8] and purified by distillation over calcium dihydride. Their purity was analyzed using gas chromatography and was higher than 99%.



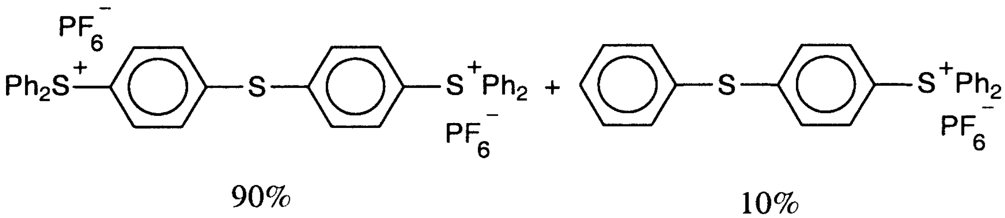
1,3-dioxolane 1,3-dioxepane 1,3,6-trioxocane

Figure 1. Cyclic acetals used as monomers

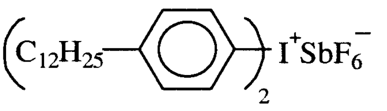
Several triarylsufonium salts, diaryliodonium salts and one iron-arene complex were used as UV photoinitiators (Figure 2).



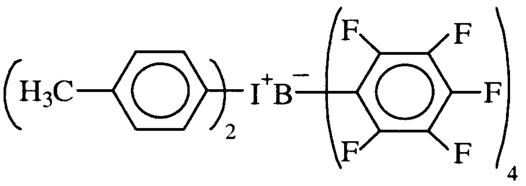
Cyracure UVI 6974



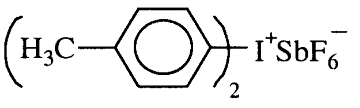
Cyracure UVI 6990



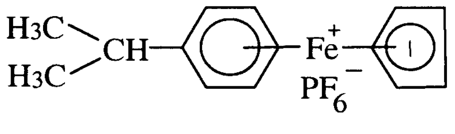
UV 9380C



TDTI



HDTI



Irgacure 261

Figure 2. Photocationic initiators

Cyracure® UVI 6974 (Union Carbide), a 50 wt% solution in propylene carbonate of a 9:1 by weight mixture of 4,4’-bis-(diphenylsulfonio)-diphenylsulfide hexafluoroantimoniate and 4-diphenylsulfonio-diphenylsulfide hexafluoroantimoniate, Cyracure® UVI 6990 (Union Carbide), the same product as UVI 6974 but containing PF_6^- as counterion and UV9380 from GE Silicones (a mixture of bis(4-dodecylphenyl) iodonium hexafluoroantimoniate, alkyl glycidyl ethers C_{12} and C_{14}, 5-10 wt% linear alkylate dodecylbenzene and i-propylthioxanthone) were stored over calcium dihydride for 24 hours. The upper clear liquid was used. The solid photoinitiators, ditolyliodonium hexafluoroantimonate - HDTI (Rhône-Poulenc), ditolyliodonium tetrakis (pentafluorophenyl borate) – TDTI (Rhône-Poulenc) and i-propylbenzene cyclopentadienyl iron hexafluorophosphate – Irgacure® 261 (Ciba Geigy) were used as received.

Procedure

Differential scanning photocalorimetry (DPC) was used as method to put in the evidence the kinetics of cationic photopolymerization of cyclic acetals. The initiation light source was a 200W high-pressure mercury lamp. Samples of 2÷4 mg were placed in aluminum DSC pans covered with a disc of polyethyleneterephtalate foil and exposed at UV light intensity in the range of 3 mW/cm^2. A number of DPC experiments were performed on cationic photopolymerization of DXL, DH and TOC with UV photoinitiators (3 wt%). A nitrogen flux of ~20 cm^3/min assured a homogeneity of temperature in the measuring cell.

Results and discussion

Polymerization

The results regarding photocationic polymerization of DXL, DH and TOC in the presence of above mentioned photoinitiators, at 30°C, are presented in Figures 3. The thermal data were transformed in conversions data by dividing the experimental enthalpies to the theoretical enthalpies, already known for monomers [9].

As it may be seen, the complex arene-iron (Irgacure 261) cannot initiate the polymerization for none of the cyclic acetals studied. On one hand, the photoinitiator is only partially soluble into the monomers, and on the other hand it decomposes efficiently only at higher temperatures.

For DXL, the most effective photoinitiators were HDTI and TDTI (ditolyliodonium salts). The triarylsufonium salt having SbF_6^-, as its anion (Cyracure UVI 6974) has been proved the most active for TOC. However we must take into account that HDTI and TDTI were only incompletely soluble in this monomer. Among the three acetals, DH is by far the most reactive. It has polymerized up to conversions higher than 80% in the presence of diaryliodonium or triarylsufonium salts.

Kinetics of polymerization

As known, polymerization of cyclic acetals may be seen as an equilibrium reaction. Accordingly, when writing the rate of monomer consumption (-d[M]/dt), we have to take into account the depropagation, respectively the equilibrium concentration.

$$-\frac{d[M]}{dt}=k_p\cdot[I^+]\cdot([M]-[M]_e) \tag{1}$$

where $[M]$ and $[M]_e$ represent monomer concentration at time t and equilibrium concentration, respectively; k_p is the rate constant for propagation, while $[I^+]$, symbolizes the concentration of active species. The values for equilibrium concentrations after 24 hours (Table 1) have been found by gas-chromatography (namely measuring the concentrations of unreacted monomer, in the absence of any solvent), according to the method previously described [7]. Equilibrium concentration for TOC at 30°C is low enough and the same value has been used during calculations for higher temperatures; we believe however, that the resulting error (in calculating rate constants) is an insignificant one. In addition, no cyclic oligomers were detected by gas-chromatography.

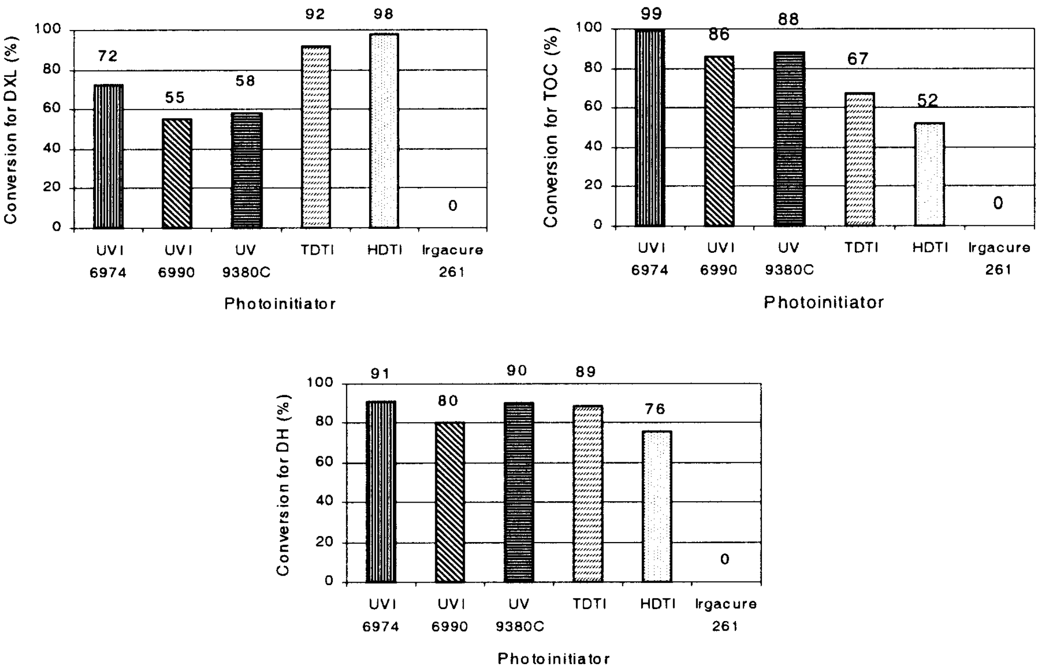


Figure 3. Conversion as function of photoinitiator for DXL, TOC and DH after 10 minutes of reaction

Table 1. Some properties of cyclic acetals

Monomers	Equilibrium Concentration (mol/L)				
	30°C	40°C	50°C	60°C	80°C
1,3-Dioxolane	1.20	1.60	2.10	2.70	-
1,3-Dioxepane	0.39	0.42	0.47	0.52	0.74
1,3,6-Trioxocane	0.10	-	-	-	-

To measure the rate constants (and subsequently the activation energies) for photocationic propagation, the three monomers (DXL, DH, TOC) have been submitted to polymerization at several temperatures, in the presence of effective photoinitiators, such as the results might present practical interest.

The only active species is proton [10]. The concentration of newly generated protons has been established by their capture with a steric hindered pyridine. Based on ^{1}H-NMR signals for protonated and non-protonated pyridine, respectively, we were able to find a linear dependence for the concentration of newly generated protons (for the triarylsulphonium salts having SbF_6^- as its anion - UVI 6974) on the received irradiation energy, and, accordingly on the exposure time.

As all photoinitiators used (diaryliodonium or triarylsufonium salts) initiate the polymerization in a similar manner as UVI 6974 [11,12], then it might be said that, in general, the concentration of newly generated protons increases in a linear form with the exposure time.

Introducing this linear dependence into the expression describing the polymerization rate, one obtains:

$$-\frac{d[M]}{dt} = k_p \cdot a \cdot t \cdot ([M] - [M]_e) \tag{2}$$

where a is a proportionality coefficient (mol/L·s), and t is the exposure time to UV radiation (s); obviously the coefficient a can take various values as a function of the nature of the photoinitiator.

After variable separation and integration, Eq. (2) becomes:

$$\ln\frac{[M]_0 - [M]_e}{[M] - [M]_e} = k_p \cdot a \cdot \frac{t^2}{2} = k_p \cdot \varphi \cdot t^2 \tag{3}$$

where $[M]_0$ represents the initial monomer concentration and $\varphi = a/2$.

Table 2. Values for φ coefficients (from Eq. 3)

Photoinitiator	φ_{DXL} [a] (mol/L·s)	φ_{DH} [b] (mol/L·s)	$\overline{\varphi}$ [c] (mol/L·s)
UVI 6974	$7 \cdot 10^{-8}$	$5 \cdot 10^{-8}$	$6{,}00 \cdot 10^{-8}$
UVI 6990	$3 \cdot 10^{-8}$	$4 \cdot 10^{-8}$	$3{,}50 \cdot 10^{-8}$
UV 9380C	$1 \cdot 10^{-7}$	$2 \cdot 10^{-7}$	$1{,}50 \cdot 10^{-7}$
HDTI	$2 \cdot 10^{-8}$	$9 \cdot 10^{-9}$	$1{,}45 \cdot 10^{-8}$
TDTI	$4 \cdot 10^{-8}$	$2 \cdot 10^{-8}$	$3{,}00 \cdot 10^{-8}$

[a] value of coefficient φ for DXL; [b] value of coefficient φ for DH; [c] average value for φ

Coefficient φ has been estimated as it follows: we knew the values k_p reported in literature [13,14] for DXL and DH at 30°C (10^2 L/mol·s for DXL and 10^3 L/mol·s for DH). The slope of the Eq. (3), gives φ coefficients for each pair monomer – photoinitiator (Figure 4), shown in the Table 2.

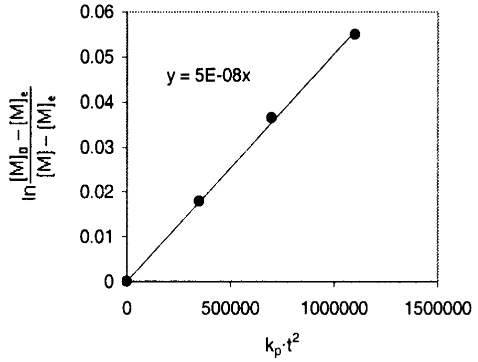
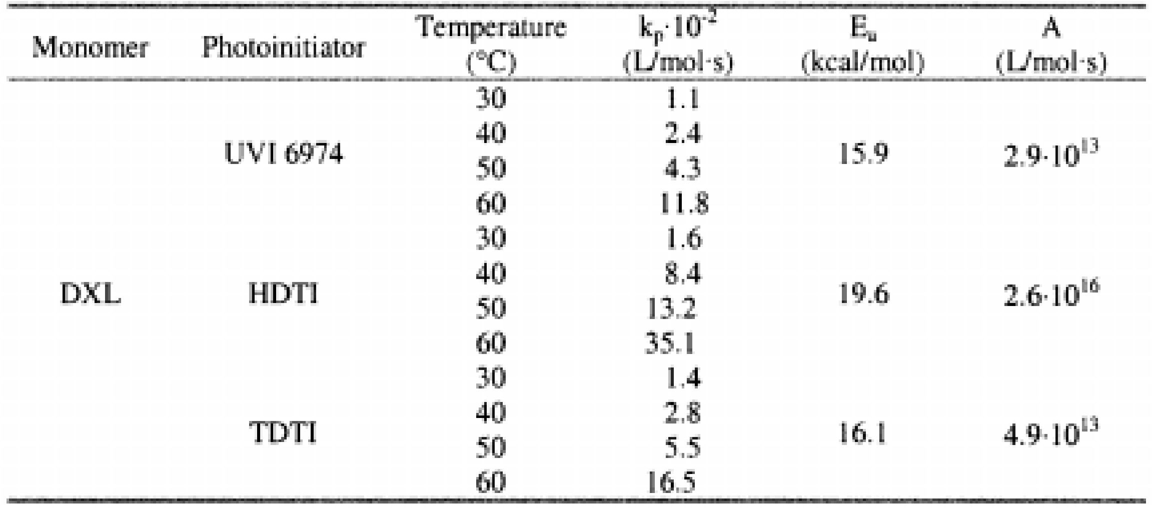


Figure 4. Value of φ coefficient from equation (3), for DH polymerization in presence of UVI 6974

The average values for *φ* were subsequently used in calculating the rate constants. Thus, knowing monomer concentration (the initial and the equilibrium ones respectively, as well as at different times *t*), we can calculate the rate constant (as the corresponding slope) from the graphical representation of Eq. 3.

According to the above mentioned kinetic model, we have calculated the rate constants for all the three cyclic acetals in the presence of some photoinitiators of practical importance (Tables 3-5). The values show similar reactivities for DH and TOC; DXL seems to be less reactive.

Table 3. The values for propagation constants, activation energies and pre-exponential factor for photo-polymerization of DXL



Monomer	Photoinitiator	Temperature (°C)	$k_p \cdot 10^{-2}$ (L/mol·s)	E_a (kcal/mol)	A (L/mol·s)
DXL	UVI 6974	30	1.1	15.9	$2.9 \cdot 10^{13}$
		40	2.4		
		50	4.3		
		60	11.8		
	HDTI	30	1.6	19.6	$2.6 \cdot 10^{16}$
		40	8.4		
		50	13.2		
		60	35.1		
	TDTI	30	1.4	16.1	$4.9 \cdot 10^{13}$
		40	2.8		
		50	5.5		
		60	16.5		

Table 4. Propagation rate constants, activation energies and pre-exponential factors for photopolymerization of TOC

Monomer	Photonitiator	Temperature (°C)	$k_p \cdot 10^{-3}$ (L/mol·s)	E_a (kcal/mol)	A (L/mol·s)
TOC	UVI 6974	30	6.1	9.6	$5.6 \cdot 10^{10}$
		40	13.4		
		50	19.0		
		60	30.3		
		80	62.4		
	UVI 6990	30	1.1	14.7	$5.2 \cdot 10^{13}$
		40	2.8		
		50	8.4		
		60	8.5		
		80	-		
	UV 9380C	30	1.1	12.6	$2.1 \cdot 10^{12}$
		40	3.8		
		50	8.9		
		60	13.7		
		80	23.1		

Table 5. Propagation rate constants, activation energies and pre-exponential factors for photopolymerization of DH

Monomer	Photonitiator	Temperature (°C)	$k_p \cdot 10^{-3}$ (L/mol·s)	E_a (kcal/mol)	A (L/mol·s)
DH	UVI 6974	30	1.6	13.2	$5.9 \cdot 10^{12}$
		40	3.1		
		50	8.3		
		60	16.4		
		80	32.1		
	UVI 6990	30	0.7	13.5	$3.8 \cdot 10^{12}$
		40	1.9		
		50	2.2		
		60	4.5		
		80	19.6		
	UV 9380C	30	1.2	13.6	$1.0 \cdot 10^{13}$
		40	4.9		
		50	6.1		
		60	17.7		
		80	32.1		
	HDTI	30	0.8	16.1	$2.4 \cdot 10^{14}$
		40	1.5		
		50	2.1		
		60	3.8		
		80	39.1		
	TDTI	30	0.6	17.2	$1.0 \cdot 10^{15}$
		40	0.9		
		50	1.9		
		60	5.4		
		80	30.7		

Activation energy

Knowing the rate constants, measured at different temperatures, the activation energies have resulted, based on Arrhenius law:

$$k_p = A \cdot e^{-\frac{E_a}{RT}} \tag{4}$$

where all parameters have the usual meaning.
The values obtained for activation energies (E_a) and pre-exponential factors (A) are presented in Tables 3-5. For all the three monomers, the lowest activation energies have been recorded in the presence of triarylsulphonium salt with SbF_6^- as anion (UVI 6974).

Conclusions

All cyclic acetals studied (DXL, DH and TOC) can polymerize using diaryliodonium and triarylsufonium salts as photocationic initiators. Differential scanning photocalorimetry (DPC) has been proved to be an efficient tool to obtain conversion versus time curves for all three monomers. For DH and TOC the most efficient photoinitiator has been proved to be UVI-6974, which represent a mixture of two salts, mono- and difunctional of triarylsulphonium with SbF_6^- as anion (10/90 by weight) and dissolved in propylene carbonate (50%). For DXL, the most efficient photoinitiator is HDTI (ditolyliodonium hexafluoroantimonate). The values for the propagation constants vary between $1.1 \cdot 10^2$ and $35.1 \cdot 10^2$ L/mol·s for DXL (in the range 30°÷60°C), between $0.6 \cdot 10^3$ and $39.1 \cdot 10^3$ L/mol·s for DH (in the domain 30°÷80°C) and, finally between $1.1 \cdot 10^3$ and $62.4 \cdot 10^3$ L/mol·s for TOC (30°÷80°C). The lowest activation energy has been recorded in the presence of UVI 6974: 9.6 kcal/mol for TOC, 13.2 kcal/mol for DH and 15.9 kcal/mol for DXL.

References

1. Kubisa P (1996) Cationic Polymerization. Mechanism, Synthesis and Application. Marcel Dekker Inc., New York
2. Hall HC Jr, Pedias AB, Atsumi M, Way TF (1988) A.C.S. Polymer Prep. 29:36
3. Vuluga DM, Pantiru M, Dimonie M, Abadie MJM (1998) Synthetic Polymer Journal 5:304
4. Vuluga DM, Pantiru M, Vasilescu DS, Dimonie M (1998) Roum. Chem. Quart. Reviews 6:293
5. Pappas SP, Photopolymerisation and Photoimaging Science and Technology (1989). Elsevier, New York
6. Crivello JV, Lam JHW, Volante CN (1977) J. Rad. Curing 4:2
7. Vuluga DM, Pantiru M, Abadie MJM (1999) Europ. Polymer J. 35:2193
8. Astle MJ, Zaslowsky JA, Lafyatis PG (1954) Ind.Eng.Chem. 46:786
9. Busfield WK (1989) Polymer Handbook. Wiley & Sons, New York, pp II/303-II/304
10. Vuluga DM, Pantiru M, Abadie MJM, unpublished data
11. Dektar JL, Hacker NP (1990) J.Org.Chem.55:639
12. Dektar JL, Hacker NP (1990) J. Amer. Chem. Soc. 112:6004
13. Penczec S (1974) Makromol. Chem. 175:1217
14. Plesch PH (1971) Adv. Polym. Sci. 8:137