## Molybdenum Carbonyl-Initiated Copolymerization of Trichloromethyl-Containing Epoxy Oligomer with Methyl Methacrylate

V. V. Kireev<sup>a</sup>, B. M. Prudskov<sup>a</sup>, S. N. Filatov<sup>a</sup>, and M. A. Tlencopatchev<sup>b</sup>

<sup>a</sup> Mendeleev University of Chemical Technology,
Miusskaya pl. 9, Moscow, 125047 Russia

<sup>b</sup> Instituto de Investigaciones en Materiales UNAM, Circuito Exterior Aportado Postal,
70-360, Mexico D.F., 04510, Mexico
e-mail: Filatovsn@list.ru

Received November 23, 2006; Revised Manuscript Received February 27, 2007

**Abstract**—Copolymers with an epoxy group content of up to 1.4% and a number-average molecular mass  $M_{\rm n} = 11\,000$  have been obtained through the copolymerization of a trichloroacetic acid-modified epoxy oligomer with methyl methacrylate in the presence of molybdenum carbonyl.

DOI: 10.1134/S0965545X0707005X

The initiation of radical polymerization of vinyl monomers with transition metal carbonyl-organohalogen compound systems opens up a possibility for regulating the rate of the process and the molecularmass characteristics of resultant polymers over wide ranges [1]. The use of chlorinated polymers, in particular, oligo(chloromethylsiloxanes), as components of initiating systems resulted in the synthesis of highmolecular-mass polyblock and grafted copolymers [2-5]. Earlier [6, 7], it was shown that polymerization of styrene, methyl methacrylate (MMA), and vinyl acetate can be initiated with Mn, Cr, and Mo carbonyls in combination with trichloromethyl-substituted compounds containing hydroxyl and epoxide groups. The presence of these functional groups does not substantially affect the process parameters and makes it possible to incorporate these groups into resultant polymers. For example, MMA polymerization in the presence of the Mn carbonyl-1,2-epoxy-4,4,4-trichlorobutane system resulted in the synthesis of high-molecular-mass PMMA containing epoxy groups both at the ends of macromolecules and as side substituents. However, 1,2-epoxy-4,4,4-trichlorobutane is an expensive compound that is not easy to obtain; therefore, it would be reasonable to replace it with another trichlorosubstituted oxirane derivatives, in particular, the product of the reaction of an epoxy oligomer with trichloroacetic acid (TCAA):

Changing the oligomer/TCAA ratio, we may widely vary the amount of trichloromethyl groups in the modified oligomer, thus controlling the number of potential sites of polymer chain growth and the amount of epoxide groups in the copolymers obtained.

Molybdenum carbonyl-initiated copolymerization of MMA with an epoxy oligomer containing trichloromethyl groups was studied in this work.

## **EXPERIMENTAL**

Experiments were performed with MMA purified of stabilizers, dried over sodium sulfate, and freshly distilled. Its parameters corresponded to published data [8]. The monomer purity was monitored by gas—liquid chromatography.

Solvents were dried according to standard procedures and used freshly distilled. Their parameters corresponded to the data reported in [9].

Molybdenum carbonyl was sublimated in vacuum.

Trichloromethyl-group-containing epoxy oligomer was synthesized via the reaction of oligomer ED-20 (epoxy equivalent weight of 187 g/equiv) with trichloroacetic acid (Merck, used as received) according to the following scheme (the scheme is presented for diphenylolpropane diglycidyl ether as an example, its content in the oligomer ED-20 is above 90%).

The reaction was carried out at different ED-20/TCAA ratios (by mass) according to preset conversions of epoxy groups (10, 20, 25, 30, 40, 50, and 100%) in a 50% toluene solution at 70°C under nitrogen for 10 h in a glass reactor equipped with a water jacket, a reflux condenser, and a magnetic stirrer. Then, the reaction mixture was washed with a 5% Na<sub>2</sub>(CO)<sub>3</sub> solution and dried over CaCl<sub>2</sub> and the solvent was distilled off in a rotary evaporator.

Trichloroacetic acid-modified epoxy oligomers (MED) thus obtained at a yield of ~96% (on the basis of total ED-20 and TCAA) were characterized by means of gel-permeation chromatography (GPC) and

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as well as by measuring the epoxide-group and chlorine contents.

MED-MMA copolymerization was performed in a 30% (relative to MMA mass) toluene solution in a glass reactor equipped with a water jacket, a reflux, and a magnetic stirrer.

A specified amount of MMA, Mo(CO)<sub>6</sub> (2.5% of MMA mass), and toluene (in an amount required to bring the MMA concentration to 30 wt %) were added to the reaction mixture resulting from the MED synthesis. The mixture was thoroughly stirred, and the reaction was carried out at 80°C for 10 h under an inert gas.

Table 1. Chlorine and epoxy-group content in the products of TCAA reaction with ED-20 (70°C, 10 h)

Modified oligomer	Preset epoxy group conversion	Content, %*			
	(by the initial TCAA amount)	epoxy groups	chlorine		
MED-10	10	20.7/18.4	5.23/2.32		
MED-20	20	18.4/12.6	9.68/4.72		
MED-25	25	17.3/10.7	11.67/6.19		
MED-30	30	16.1/8.3	13.52/8.80		
MED-40	40	13.8/5.4	16.86/-		
MED-50	50	11.5/3.2	19.79/15.29		
MED-100	100	0	30.36/25.80		

<sup>\*</sup> The figures in the numerator and denominator are the calculated and measured values, respectively.

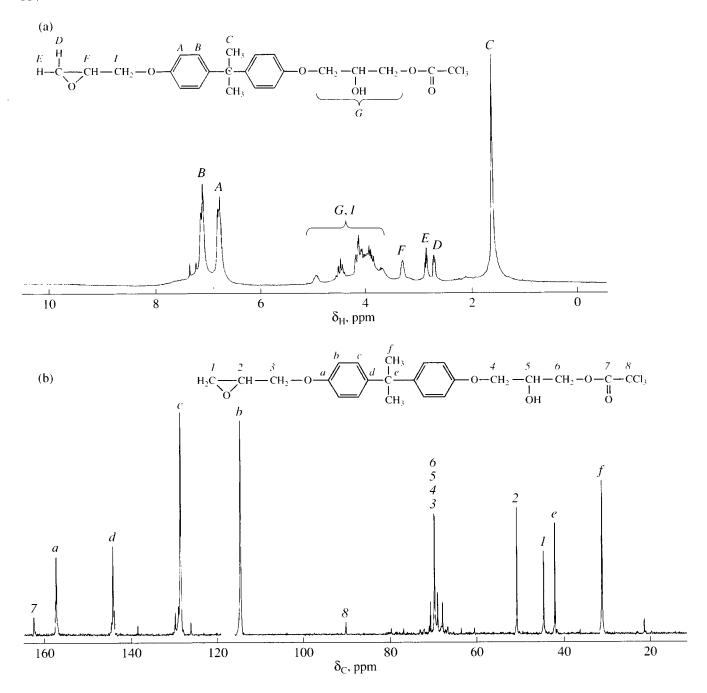


Fig. 1. The (a) <sup>1</sup>H and (b) <sup>13</sup>C NMR spectra of modified epoxy oligomer MED-50.

Obtained copolymers were precipitated into isopropanol (tenfold excess) and reprecipitated from toluene into petroleum ether. The copolymers were washed with the precipitant and dried in vacuum at 70°C and at a residual pressure of 1.3 kPa.

GPC analysis was performed with a Waters 1500 instrument, a 30 cm column, Ultrastyragel with pore sizes of 10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup> Å as a solid phase, a UV spec-

trophotometer ( $\lambda$  = 264 nm) and a refractometer as detectors, and THF as an eluent. The elution rate was 1 ml/min.

Molecular masses were measured by osmometry with a Knauer K-7000 vapor-pressure osmometer.

The <sup>13</sup>C and <sup>1</sup>H NMR spectra were measured with a Bruker CXP-200 spectrometer operating at frequencies of 50.3 and 200 MHz, respectively.

**Table 2.** The yield and some characteristics of MMA–MED copolymers (80°C, 10 h, 2.5 wt % of Mo(CO)<sub>6</sub> relative to MMA, MMA: MED = 1:1, mass/mass)

Initial MED (according to Table 1)	Yield, %, on total MED and MMA basis*	Content, %					The average number	
		epoxy groups	chlorine**	$M_{\rm n}^{***} \times 10^{-3}$	$M_{\rm w} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$	of MMA units per one MED fragment	
MED-10	66	1.4	0.484	8.6	25.8	3.0	14	
MED-20	61	1.3	_	7.7	29.1	3.8	9	
MED-30	65	0.4	0.750	11.9	37.0	3.1	9	
MED-40	82	0.6		15.2	37.0	2.4	15	
MED-50	77	0.3	_	7.4 (4.2)	92.3	12.5	5	
MED-100	$\frac{49}{58}$	-	$\frac{6.045}{10.200}$	8.0 (9.7)	22.1	2.7	13	

<sup>\*</sup>The numerator and denominator refer to the yield of the soluble fraction whose molecular mass values are presented and the total copolymer yield, respectively

Table 3. The yield and some characteristics of MMA–MED-30 copolymers (2.5 wt % Mo(CO)<sub>6</sub> relative to MMA, 80°C, 10 h)

t no.	Q	, % on total and MMA		Epoxy group content, %					mber iits roup
Experimen	Experiment no.  MMA/MED  mass ratio  Yield, % on tota  MED and MM/ basis	Yield, % of MED and I basis	Chlorine content, %	calculated*	observed**	$M_{\rm n}^{***} \times 10^{-3}$	$M_{\rm w} \times 10^{-3}$	$M_{\rm w}/M_{\rm n}$	Average number of MMA units per epoxy group
1	1:0.5	78	_	_	<u>0.2</u> 1.9	29.4 (11.0)	51.3	1.75	54
2	1:1.0	65	0.750	0.5	<u>0.4</u> <u>2.9</u>	11.9 (5.8)	37.0	3.10	9
3	1:1.5	34	2.830	1.7	0.9 3.7	10.2	26.4	2.60	4
4	1:2.0	31	2.250	1.4	1.4 4.6	7.3 (3.6)	21.1	2.89	7

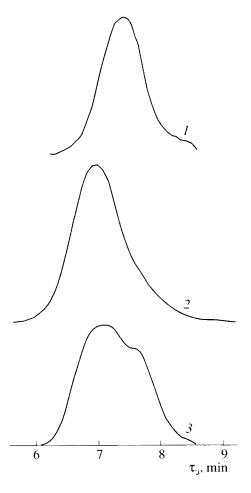
<sup>\*</sup>As calculated under the condition that one epoxy group corresponds to two chlorine atoms.

<sup>\*\*</sup>The numerator and denominator refer to the chlorine contents in the soluble and gel fractions, respectively.

<sup>\*\*\*</sup>Parenthesized values refer to  $M_n$  measured by osmometry

<sup>\*\*</sup>The numerator and denominator refer to the values obtained after and before the copolymer precipitation.

<sup>\*\*\*</sup>Parenthesized values refer to  $M_n$  measured by osmometry

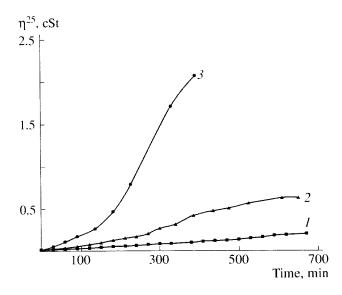


**Fig. 2.** Gel-permeation chromatograms of epoxy oligomer–MMA copolymers. The curve numbers correspond to the numbering of copolymers in Table 3.

The epoxy-group and chlorine contents were determined by mercurimetric [10] and X-ray fluorescence analyses, respectively.

## RESULTS AND DISCUSSION

The reaction between ED-20 and TCAA affords oligomers with different contents of epoxy and trichlo-

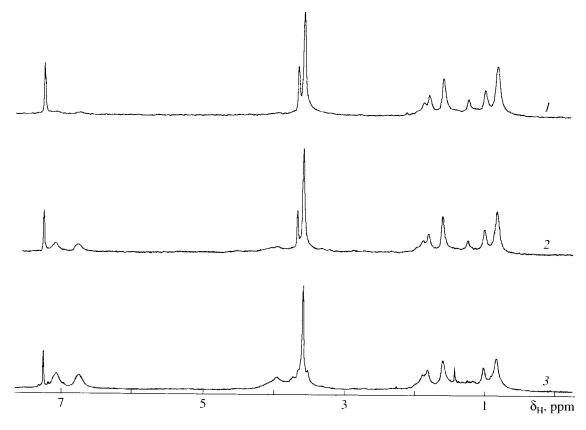


**Fig. 3.** Time variations in the viscosity of an MMA–MED-30 reaction mixture (Table 3, experiment 2). MMA contents in the toluene solutions are (1) 20, (2) 25, and (3) 30%.

romethyl groups (Table 1). In the presence of molybdenum carbonyl, the trichloromethyl groups form radicals, which initiate MMA polymerization. As the amount of TCAA taken for the esterification is increased, the average molecular mass of the oligomers rises and the relative amount of epoxy groups decreases (Table 1).

The  $^{13}$ C and  $^{1}$ H NMR spectra of the product of the epoxy oligomer reaction with TCAA (Fig. 1) exhibit signals at  $\delta_{\rm C}$  = 90.05 and 163 ppm due to carbon atoms of CCl<sub>3</sub> and C=O groups, respectively, and signals at  $\delta_{\rm H}$  = 2.0–2.5 ppm assigned to protons of epoxy groups that were not involved in the reaction with TCAA.

Presumably, the copolymerization of MMA with trichloromethyl-group-modified epoxy oligomers may be schematically represented as follows.



**Fig. 4.** The <sup>1</sup>H NMR spectra of MED–MMA copolymers. The numbering of the spectra correspond to that of the copolymers in Table 3.

The copolymerization of MMA with trichloromethyl-group-containing epoxy oligomers in the presence of molybdenum carbonyl gives rise to the formation of copolymers with a yield of 30–80% relative to the sum of MMA and MED (Tables 2, 3). The decreased yield of the copolymers is due to both an incomplete incorporation of MED into them and the presence of residual molecules of intact oligomer ED-20 free of trichloromethyl groups in the product. These oligomers are removed when the copolymerization product is precipitated into isopropanol.

The polymerization proceeds neither in the MED–MMA system free of molybdenum carbonyl nor in the MMA–carbonyl system free of trichloromethyl compounds; hence, the homopolymer PMMA is not formed in the MED–MMA–Mo(CO)<sub>6</sub> system under examination. In addition, the absence of the homopolymer from the reaction mixture is confirmed by the unimodal pattern of GPC curves (Fig. 2), whereas a control PMMA + MED mixture is characterized by a bimodal GPC curve.

The weight-average molecular mass  $M_{\rm w}$  of the formed copolymers rises with an increase in the amount of trichloromethyl groups in MED. According to the above polymer formation scheme, a rise in the amount of trichloromethyl groups in MED increases the num-

ber of radicals that initiate MMA polymerization, thereby supposedly leading to a reduction in the molecular mass; however, this is not the case, as shown by the data in Table 2. In our opinion, as the amount of terminal trichloromethyl groups rises, the molecular mass increases as a result of the reinitiation reaction involving molybdenum carbonyl and chlorine atoms of any macromolecule present in the reaction mixture. The reinitiation by the action of a transition metal carbonylhalogenated organic compound system was repeatedly shown earlier for MMA polymerization [3, 6, 7].

Block copolymers with different contents of epoxy groups were obtained by copolymerizing the modified oligomers at different MED/MMA mass ratios (Table 3).

As was shown by the example of MED-30, when its relative amount in the reactant mixtures with the monomer increases, the molecular mass of the resultant copolymers decreases somewhat (Table 3). Seemingly, the effect of dilution of the reaction mixture with increasing amounts of the inert MED-30 fraction free of trichloromethyl groups prevails over the reinitiation effect in this case. In addition, a reduction in the copolymer yield is caused by a rise in the relative amount of the epoxy oligomer that is not involved in the copolymerization and is removed by the reprecipitation.

The optimal molybdenum content ranges from 2 to 5% of the monomer mass; the copolymer yield is low below 2% and insoluble products are formed above 5%.

Variations in the viscosity of the reaction mixture during copolymerization (Fig. 3) demonstrate that the optimal duration of the process is 10 h. Its further increase leads to the formation of a crosslinked polymer.

The <sup>1</sup>H NMR spectra of the obtained copolymers (Fig. 4) comprise groups of signals at 6.5–7.3 and 3.3–3.8 ppm due to aryl protons of epoxy oligomers and protons of OCH<sub>3</sub> groups in PMMA chains, respectively. As the relative amount of MMA is increased, the intensity of the signals assigned to aryl group protons declines (Fig. 4). From the integral intensities of the signals in the <sup>1</sup>H NMR spectra, the ratio between MMA and aromatic fragments in copolymer molecules was calculated, and the average number of MMA groups per one MED fragment was determined (Tables 2, 3).

The low average numbers of MMA units per one MED fragment, as compared to the molecular masses of the resultant copolymers, suggest that MED is predominantly incorporated into polymer chains as side branches resulting from the reinitiation reactions.

The copolymers obtained with different epoxygroup contents are of interest as compatibilizing agents for epoxy oligomers regulating the properties of epoxy composites. On the other hand, the application of trichloromethyl-substituted epoxy oligomers as coinitiators of vinyl monomer polymerization allows incorporate oxiranion of cycles into resultant polymers with the purpose of subsequent immobilization of dye molecules or molecules of biologically active substances.

## **REFERENCES**

- 1. C. H. Bamford, *Reactivity, Mechanism and Structure in Polymer Chemistry*, Ed. by A. D. Jenkins and A. Ledwith (Wiley, New York, 1976).
- O. V. Shkol'nik, A. F. Fedotov, E. I. Blokhina, et al., Vysokomol. Soedin., Scr. A 30, 1759 (1988).
- V. V. Kireev, B. M. Prudskov, and M. Yu. Komarova, Polymer Science, Ser. A 40, 394 (1998) [Vysokomol. Soedin., Ser. A 40, 728 (1998)].
- 4. D. W. Jenkins and S. M. Hudson, Macromolecules 35, 3413 (2002).
- Y. Shirai, K. Kawatsura, and N. Tsubokawa, Prog. Org. Coat. 36, 217 (1999).
- V. V. Kireev, B. M. Prudskov, V. A. Polyakov, et al., Polymer Science, Ser. A 46, 1307 (2004) [Vysokomol. Soedin., Ser. A 46, 1989 (2004)].
- 7. V. V. Kireev, B. M. Prudskov, S. N. Filatov, and O. L. Lipendina, Polymer Science, Ser. B 48, 138 (2006) [Vysokomol. Soedin., Ser. B 48, 1024 (2006)].
- 8. V. A. Rabinovich and Z. Ya. Khavin, *Abridged Chemical Dictionary* (Khimiya, Leningrad, 1977) [in Russian].
- 9. A. Weissberger, E. Proskauer, J. Riddick, and E. Toops, Organic Solvents. Physical Properties and Methods of Purification (Wiley, New York, 1955; Inostrannaya Literatura, Moscow, 1958).
- M. F. Sorokin and K. A. Lyalyushko, Laboratory Works on Chemistry and Technology of Film-Forming Compounds (Khimiya, Moscow, 1971) [in Russian].