

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

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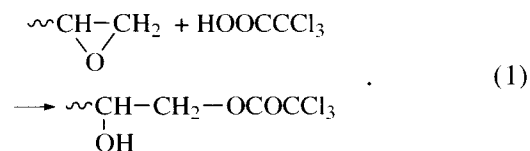
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Abstract—Copolymers with an epoxy group content of up to 1.4% and a number-average molecular mass $M_n = 11000$ have been obtained through the copolymerization of a trichloroacetic acid–modified epoxy oligomer with methyl methacrylate in the presence of molybdenum carbonyl.

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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 molecular-mass 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 high-molecular-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.

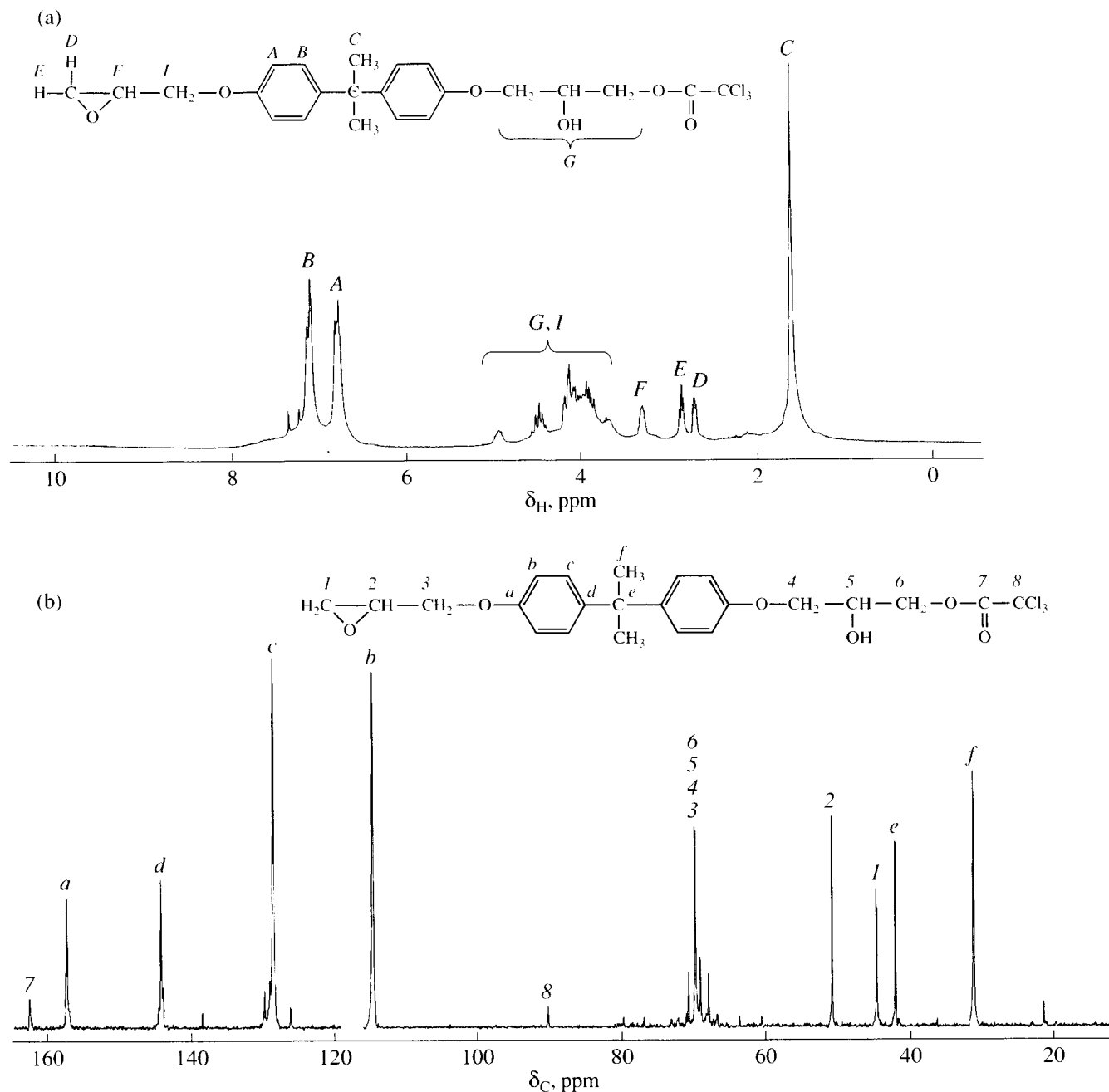


Fig. 1. The (a) ¹H and (b) ¹³C NMR spectra of modified epoxy oligomer MED-50.

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, Ultrastaygel with pore sizes of 10³, 10⁴, and 10⁵ 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 ¹³C and ¹H 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)₆ relative to MMA, MMA : MED = 1 : 1, mass/mass)

Initial MED (according to Table 1)	Yield, %, on total MED and MMA basis*	Content, %		$M_n^{***} \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	The average number of MMA units per one MED fragment
		epoxy groups	chlorine**				
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

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

**The numerator and denominator refer to the chlorine contents in the soluble and gel fractions, respectively.

***Parenthesized values refer to M_n measured by osmometry

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

Experiment no.	MMA/MED mass ratio	Yield, % on total MED and MMA basis	Chlorine content, %	Epoxy group content, %		$M_n^{***} \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	Average number of MMA units per epoxy group
				calculated*	observed**				
1	1 : 0.5	78	–	–	$\frac{0.2}{1.9}$	29.4 (11.0)	51.3	1.75	54
2	1 : 1.0	65	0.750	0.5	$\frac{0.4}{2.9}$	11.9 (5.8)	37.0	3.10	9
3	1 : 1.5	34	2.830	1.7	$\frac{0.9}{3.7}$	10.2	26.4	2.60	4
4	1 : 2.0	31	2.250	1.4	$\frac{1.4}{4.6}$	7.3 (3.6)	21.1	2.89	7

*As calculated under the condition that one epoxy group corresponds to two chlorine atoms.

**The numerator and denominator refer to the values obtained after and before the copolymer precipitation.

***Parenthesized values refer to M_n measured by osmometry

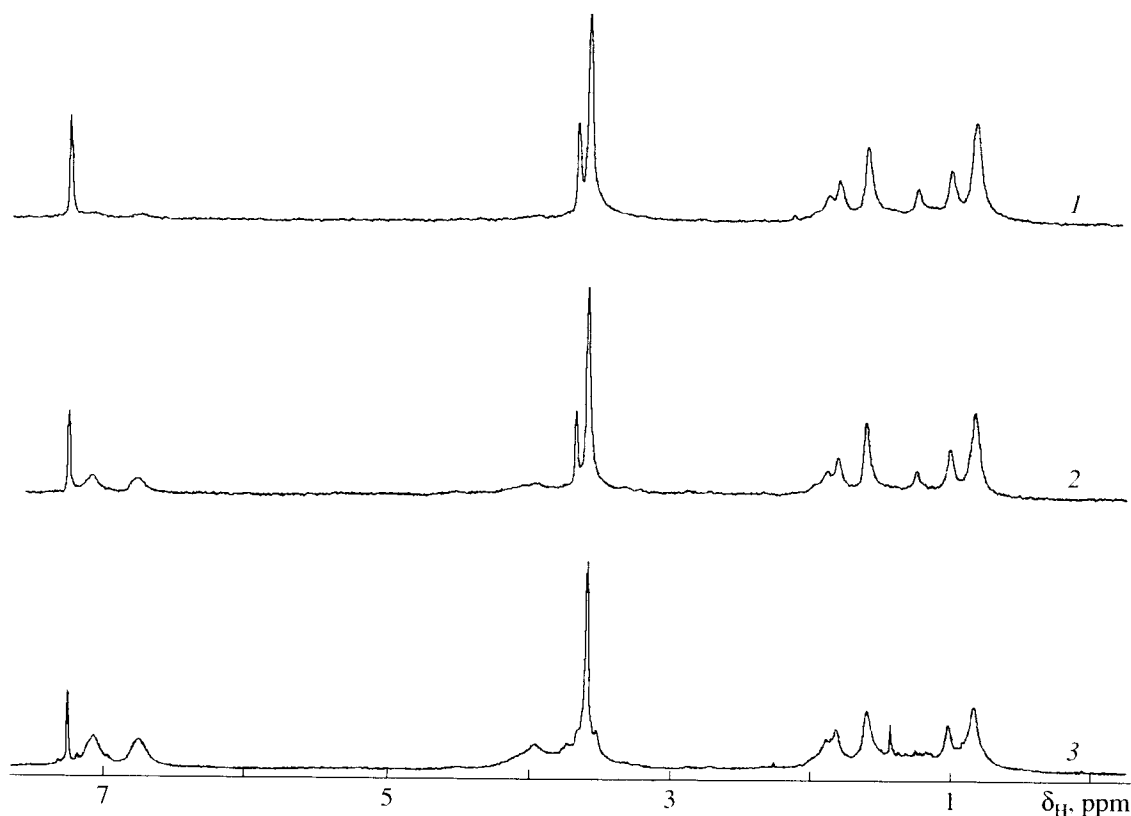


Fig. 4. The ^1H NMR spectra of MED-MMA copolymers. The numbering of the spectra correspond to that of the copolymers in Table 3.

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)₆ 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_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 carbonyl-halogenated 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 ^1H 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_3 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 ^1H 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 epoxy-group 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 oxirane of cycles into resultant polymers with the

purpose of subsequent immobilization of dye molecules or molecules of biologically active substances.

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