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Abstract

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G. D. RUDKOVSKAYA, T. A. SOKOLOVA,
Corresponding Member of the Academy of Sciences of the USSR M. M. KOTON

ON THE STRUCTURE OF POLY-DIMETHACRYLAMIDES

The literature contains data indicating that symmetrical divinyl compounds of the type of acrylic and methacrylic acid anhydrides ($^{1-4}$) and 1,6-substituted heptadienes (^{5}) form linear polymers with six-membered rings in the chain.

In studying linear cyclic polymers of a series of dimethacrylamides (^{6,7})

$$CH_2 = C(CH_3) - CO - N(R) - CO - C(CH_3) = CH_2,$$

we set ourselves the task of establishing the structure of these polymers.

Analogous polymers can be obtained by reactions in the chains of poly-methacrylamides ($^{6-8}$). In the partial thermal deamination of these polymers, the formation of only a six-membered repeating unit is conceivable,

$$\text{six-membered unit in the poly-methacrylamide chain} \xrightarrow{-NH_2R} \text{six-membered cyclic imide unit}$$

where

$$R = -H;\ -CH_3;\ -C_2H_5;\ -C_3H_7;\ -C_6H_5.$$

In the polymerization of monomers of the dimethacrylamide series, one may envisage the formation of two different cyclic structures: five- or six-membered, depending on the mode of addition of the second vinyl group at the stage of intramolecular chain growth: head-to-tail (I) or head-to-head (II).

$$\text{dimethacrylamide monomer unit} \longrightarrow \begin{cases} \text{six-membered cyclic structure} \\ \text{(I)} \\ \text{five-membered cyclic structure} \end{cases}$$

$$R = -CH_3;\ -C_2H_5;\ -C_3H_7;\ -C_6H_5.$$

The structure of the polymers obtained was established by the method of IR spectroscopy. Comparison of the IR spectra of polymers obtained by polymerization of monomers of the dimethacryloyl series and of polymers formed during partial thermal deamination of the corresponding poly-methacrylamides showed that, in the absorption region of the carbonyl group, substantial differences are observed in the IR spectra.

For polymers obtained by polymerization of the corresponding N-substituted dimethacrylamides, carbonyl absorption appears in the region 1700–1790 cm^{-1}. For polymers obtained by thermal deamination of poly-methacrylamides, the carbonyl absorption region is shifted toward longer wavelengths: 1670–1730 cm^{-1} (see Table 1).

Since the IR spectra of poly-N-alkyl-(aryl)-dimethacrylamides differ from the spectra of the corresponding deaminated polymers, it follows—

Table 1

IR spectra of polymers (absorption bands of the $C = O$ group in cm^{-1})

No.	Polymers obtained by polymerization of monomeric dimethacrylamides	$C = O$ (cm^{-1}) 1	$C = O$ (cm^{-1}) 2	Difference (cm^{-1})	No.	Polymers obtained by partial deamination of poly-methacrylamides	$C = O$ (cm^{-1}) 1	$C = O$ (cm^{-1}) 2	Difference (cm^{-1})
1	$R = -CH_3$	1705	1778	73	1′	$R = -CH_3$	1672	1722	50
2	$-C_2H_5$	1702	1772	70	2′	$-C_2H_5$	1667	1718	51
3	$-C_3H_7$	1705	1775	70	3′	$-C_3H_7$	1668	1720	52
4	$-C_6H_5$	1715	1787	72	4′	$-C_6H_5$	1680	1730	50
5	$R = H$	1700	1755	55	5′	$-H$	1695	1755	60

that, as a result of deamination, a polymer containing six-membered rings is obtained, whereas polymerization of divinyl monomers gives a polymer with five-membered cycles in the main chain.

To prove this assumption, the regions of carbonyl absorption in the IR spectra of five-membered and six-membered cyclic imides used as models were examined (see Table 2). From the data in Table 2 it is evident that the region of carbonyl absorption in the IR spectra of five-membered cyclic imides lies within 1700–1780 cm^{-1}. The carbonyl absorption region in the spectra of six-membered cyclic imides is shifted toward longer wavelengths (1680–1740 cm^{-1}).

Also noteworthy is the fact that the difference (in cm^{-1}) between the two carbonyl absorption bands in model five-membered imides (Table 2) is a constant quantity and amounts to 68–75 cm^{-1}, which agrees well with the difference in the positions of the carbonyl absorption bands in the IR spectra of poly-N-substituted dimethacrylamides, equal to 70–78 cm^{-1}. The difference between the absorption bands of the $C = O$ groups in six-membered cyclic imides (Table 2) is 52–55 cm^{-1}, which coincides with the difference in band positions in the IR spectra of polymers obtained by deamination of the corresponding poly-methacrylamides.

Thus, during polymerization of N-substituted dimethacrylamides, cyclic polymers containing predominantly five-membered rings are obtained, whereas deamination of the corresponding poly-methacrylamides gives polymers with repeating six-membered cyclic units.

Table 2

IR spectra of model compounds

No.	Five-membered cyclic imides	$>C=O$ (cm^{-1}) 1	$>C=O$ (cm^{-1}) 2	Difference (cm^{-1})	No.	Six-membered cyclic imides	$>C=O$ (cm^{-1}) 1	$>C=O$ (cm^{-1}) 2	Difference (cm^{-1})
1	$R = -CH_3$	1700	1770	70	1	cyclic imide structure: $(CH_2)_3(CO)_2NH$ *	1694	1746	52

No.	Five-membered cyclic imides	$>C=O$ (cm^{-1}) 1	$>C=O$ (cm^{-1}) 2	Difference (cm^{-1})	No.	Six-membered cyclic imides	$>C=O$ (cm^{-1}) 1	$>C=O$ (cm^{-1}) 2	Difference (cm^{-1})
2	$-C_6H_5$	1712	1780	68	2	cyclic imide structure: $\sim CH{-}CH_2\sim$ ring with CH_2, two CO, and NH *	1686	1740	55
3	$-H$	1700	1774	74					
4	polymer-chain five-membered imide unit with CH_3 substituents	1703	1779	76					

* According to (9).

The exception in this series is unsubstituted dimethacrylamide. The polymer obtained by polymerization of the monomer and the polymer formed as a result of deamination of polymethacrylamide have identical IR spectra and, consequently, are identical in their structure (see Fig. 1). These polymers contain six-membered rings linked to one another by methylene bridges.

Experimental Part

1. Polymerization of phenyldimethacrylamide (PDMA). Weighed portions of PDMA and benzoyl peroxide (B.P.) (0.2-0.15 wt. %) were placed in an ampoule. After sealing the ampoule in an atmosphere of argon (or air), its contents were melted and heated at a temperature of 85-100° for 1-10 days.

The conversion reached 50–75%.

Fig. 1. IR spectrum of polydimethacrylamide obtained by polymerization of the monomer (A), and of the same polymer obtained by deamination of polymethacrylamide (B).

The polymer samples obtained are soluble in most organic solvents and do not dissolve in water or alcohol. The intrinsic viscosity for different samples is $[\eta] = 0.1$–0.35 (in chloroform). The maximum molecular weight, determined by the thermistor method, is 10,000; softening point 185° (by IBC).

2. Polymerization of propylmethacrylamide (PMA). Weighed portions of PMA (m.p. 28°) and dinitrile of azoisobutyric acid (DINA) (0.3 wt. %) were placed in an ampoule. After sealing the ampoule in an atmo-

in an argon atmosphere, it was irradiated with UV light (PRK-2 lamp) at a temperature of 30–35° for 10 days. The polymer obtained is soluble in most organic solvents; it is insoluble in water and alcohol.

Conversion 27%, $[\eta]$ in acetone 0.16.

3. **Polymerization of dimethacrylamide (DMA)** was carried out in benzene solution (polymerization in bulk gives an insoluble polymer), at a monomer concentration of 16% with 0.2 wt.% DINITRILE, by heating at 65° for 7 hr in an argon atmosphere.
4. **Deamination of poly-methacrylamide** was carried out at 300° for 1.5 hr in vacuum at a residual pressure of 2–3 mm Hg (6; 7; 8).

IR spectra were recorded in KBr pellets by E. I. Pokrovsky and E. F. Fedorova on a Nippon Bunko DS-21 instrument, NaCl prism, for which the authors express their gratitude.

Institute of Macromolecular Compounds
Academy of Sciences of the USSR

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CITED LITERATURE

1. A. Crawshaw, G. B. Butler, J. Am. Chem. Soc., **80**, 5464 (1958).
2. J. F. Jones, J. Polym. Sci., **33**, 15 (1958).
3. T. Muike, J. Chem. Soc. Japan, **64**, 710 (1961).
4. J. Meicier, G. Smets, J. Polym. Sci., **1A**, No. 5, 1491 (1963).
5. C. S. Marvel, R. D. Vest, J. Am. Chem. Soc., **79**, No. 21, 5771 (1957).

6. T. A. Sokolova, T. D. Rudkovskaya, Vysokomolek. soed., **3**, 706 (1961).

7. T. A. Sokolova, T. D. Rudkovskaya, Vysokomolek. soed., collection *Carbocyclic Compounds*, **4**, 166 (1963).

8. G. M. Chetyrkina, T. A. Sokolova, M. M. Koton, Vysokomolek. soed., collection *Carbocyclic Compounds*, **4**, 213 (1963).

9. T. Muike, J. Chem. Soc. Japan, **64**, 359 (1961).

Note: Figure translations are in progress. See original paper for figures.