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TAUTOMERIC EQUILIBRIUM AND POLYMERIZATION ACTIVITY OF METHACRYLOYL ACETONE*

V. V. KOPEIKIN, YE. F. PANARIN, I. S. MILEVSKAYA and N. S. REDI

Institute of High Molecular Weight Compounds, U.S.S.R. Academy of Sciences

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A study was made of copolymerization of unsaturated acyclic β -diketone-methacryloyl acetone with N-vinylpyrrolidone, acrylonitrile and styrene. Copolymerization constants and the Alfrey-Price parameters were determined for these pairs of comonomers. It was found that the tautomeric equilibrium of methacryloyl acetone influences its behaviour in copolymerization which was confirmed by experimental results of copolymerization, a quantum chemical calculation related to tautomers and a comparison of their polymerization activity with model compounds.

THE synthesis of new water soluble copolymers containing reactive functional groups is now an important problem. Copolymers containing β -dicarbonyl groups may be used in particular as polymer matrices for the addition of biologically active substances [1] and as chelate forming resins with specific affinity for some metal ions [2].

With the appearance of new methods for the synthesis of unsaturated β -dicarbonyl compounds [3, 4], monomers of this type are becoming more readily avail-

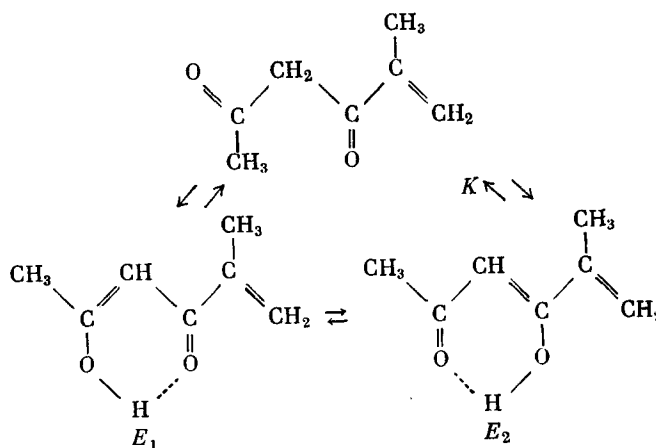
* *Vysokomol. soyed.* **A19**: No. 4, 861-866, 1977.

able. However, there is no quantitative information in the literature so far about polymerization activity. It is known [5] that 1-hexene-2-methyl (3,5-dion(methacryloyl acetone) (MAC)) is a monomer of this type, which has been studied in most detail and which is readily copolymerized with several vinyl monomers.

This paper is the first attempt to evaluate quantitatively the activity of this monomer in copolymerization.

We have previously made a quantitative evaluation of the contents of MAC tautomers in an equilibrium mixture at different temperatures and derived thermodynamic functions of keto-enol [6] and enol intra-chelate transition [7]. Enthalpy and entropy values of these transitions were 3391.0 ± 12.0 ; 645.0 ± 5.0 cal/mole and 6.97 ± 0.02 ; 0.69 ± 0.02 cal/mole·deg., respectively.

In contrast to β -dicarbonyl compounds previously examined, for example acetyl acetone, it was found for MAC that NMR chemical shifts of ^{13}C depend on temperature. This behaviour of the compound clearly confirms the existence of energetically non-equivalent chelate states for MAC. The temperature dependence of the composition of equilibrium mixture obtained from experimental results [7] is shown in the Figure in terms of potential energy. The distribution of tautomers in the equilibrium mixture is as follows

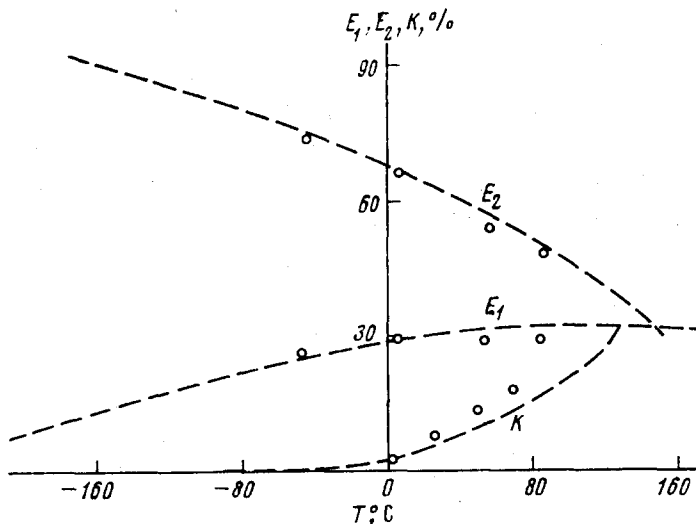


It may be seen that cooling the equilibrium mixture results in an enrichment of the mixture with the enol form E_2 and a reduction of the proportion of ketone form K . The proportion of the tautomer E_1 over a wide range of temperature, however, remains practically unchanged. This fact does not confirm the stability of the tautomer E_1 . The loss of tautomer E_1 , on reducing temperature is, apparently, partially offset by its formation from keto-form K , until it is used up completely. This assumption is confirmed by the qualitative agreement of experimental results concerning the composition of the equilibrium mixture and calculated values.

Apart from temperature the composition of the equilibrium mixture of methacryloyl acetone is affected by the variation of medium polarity. However, the

absolute proportion of tautomers shows little variation. Thus, when studying 10% MAC solutions in CCl_4 and acetone approximately the same effect is observed—the proportion of enol forms increases by 4 and 5%, respectively compared with pure MAC.

It could be expected that the tautomeric equilibrium of MAC has a considerable influence on behaviour during copolymerization. The system undergoing copolymerization in the general case contains four components—a vinyl comonomer and three MAC tautomers, their ratio depending both on temperature and the polarity of the comonomer partner. It is possible that MAC tautomers have a variable reactivity and take part to a varying extent in this chemical reaction and



Effect of temperature on the tautomeric composition of MAC; circles show experimental results; the broken line shows calculation curves.

their loss is offset by a corresponding shift of the tautomeric equilibrium. All these factors involve some difficulties in determining the composition of the initial monomer mixture. On the other hand, the composition of the copolymers formed also gives little information about the part of some tautomer in copolymerization since tautomeric equilibrium of specific type exists in the polymer [8] and the evaluation of the contents of enol forms is not reliable enough in view of the diffuse nature of PMR signals in spectra of these copolymers.

Considering the difficulties involved in evaluating the part of various tautomers of MAC in copolymerization, constants of copolymerization were calculated without considering the tautomeric equilibrium of MAC. Copolymerization constants derived by the Finemann–Ross method [9] were thus an overall reflection of processes taking place during copolymerization of MAC with vinyl monomers, such as N-vinylpyrrolidone (VP), acrylonitrile (AN) and styrene (St) (Table 1).

Copolymerization constants r derived from experimental results and semi-empirical values of activity Q and polarity of monomers e calculated from the Alfrey-Price equations [10], are shown in Table 2.

TABLE 1. COPOLYMERIZATION OF METHACRYLOL ACETONE

Molar ratio of MAC in a M_1 monomer mixture	Molar ratio of MAC in the copolymer according to analytical results m_1	Calculated molar proportion of MAC in the copolymer m_1	Time of copolymerization, min	Yield, %
N-Vinylpyrrolidone				
0.6550	0.9180	0.9173	150	9.8
0.4470	0.8425	0.8392	180	8.2
0.2800	0.7436	0.7462	210	7.7
0.1450	0.6290	0.6311	210	5.5
0.0480	0.4690	0.4766	360	9.3
Acrylonitrile				
0.6682	0.8930	0.8912	150	6.5
0.4916	0.8192	0.8152	180	6.6
0.3020	0.7140	0.7119	150	3.7
0.2000	0.6397	0.6419	180	3.0
0.0358	0.4423	0.4467	300	7.5
Styrene				
0.6693	0.8100	0.8096	150	6.7
0.5377	0.7311	0.7343	150	5.9
0.3000	0.5903	0.5883	120	6.0
0.1683	0.4810	0.4819	150	7.1
0.0500	0.2873	0.2867	180	9.5

Values of Q_2 and e_2 for VP, AN and styrene were taken from the literature [11]. Different values of Q_1 and e_1 for MAC obtained by calculation in first approximation confirmed the part of various tautomeric forms of MAC in copolymerization. Thus, resonant energies of stabilization of radical Q_1 showed a considerable dif-

TABLE 2. COPOLYMERIZATION PARAMETERS OF METHACRYLOYL ACETONE

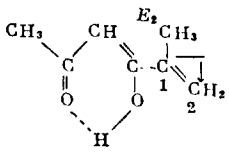
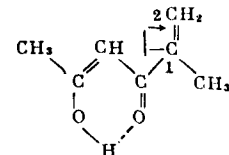
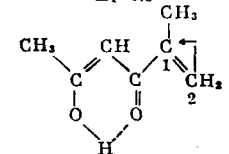
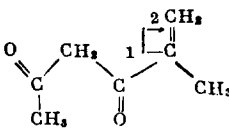
M_1	M_2	r_1	r_2	e_1	Q_1	e_2	Q_2
MAC	VP	5.38 ± 0.05	0.020 ± 0.005	0.35	1.3	-1.14	0.14
„	AN	3.60 ± 0.06	0.015 ± 0.005	-0.51	5.1	1.20	0.60
„	St	1.70 ± 0.04	0.090 ± 0.005	0.57	3.7	-0.80	1.00

ference in copolymerization of MAC with different comonomers, which proves a varying degree of electron delocalization on the methacryloyl acetone double bond. The value of e_1 for MAC changed sign, which confirmed a marked difference in donor-acceptor properties of the β -dicarbonyl group for various MAC tautomers.

An analysis of results suggests that a MAC tautomer with an electron acceptor substituent copolymerizes with comonomers having electron donor substituents at the double bond (styrene, N-vinylpyrrolidone) and a tautomer with an electron donor substituent copolymerizes with acrylonitrile.

In order to answer the question of the part of some MAC tautomer in copolymerization with a vinyl monomer, MAC tautomers were subjected to quantum chemical calculation by a method fully disregarding differential overlap. This cal-

TABLE 3. SOME CHARACTERISTICS OF MAC TAUTOMERS

Conformation of MAC tautomer	Total energy of molecules, kcal/mole	Dipole moment, Debye	Charges on carbon atoms of the vinyl group of MAC		Molecular fraction in the equilibrium mixture at 65°
			C ₁	C ₂	
 E_2 -trans	-59024.133	4.212	-0.005	-0.010	0.512
 E_1 -cis	-59020.880	4.307	-0.004	-0.022	0.300
 K	-59020.834	4.094	-0.012	-0.008	
	-59008.676	4.704	-0.004	-0.023	0.188

culatation of enol tautomers of MAC has been carried out previously [6]. An analysis of molecular diagrams of conformers of an enol tautomer E_1 showed that the mutual position of carbonyl and vinyl groups in space has a marked effect on the distribution of electron density on the double bond of this MAC tautomer. Thus, the conformer with a vinyl group in the *cis*-position in relation of the carbonyl

group had an electron shortage on the double bond of the vinyl group, compared with the conformer, for which the vinyl and carbonyl groups were in the *trans*-position in relation to each other.

Calculation was made in this study in relation to a MAC tautomer of diketone type; possible stereo-isomers obtained by the rotation of acetyl and methacryloyl groups round a carbon-carbon bond were examined. It appeared that of several tautomer conformers of diketone type a conformer with *trans*-position of carbonyl groups in relation to the carbon chain is the most favourable from an energy point of view. Quantum chemical calculation of MAC tautomers enabled tautomer conformations most favourable from an energy point of view to be established, some characteristics of which are shown in Table 3. This Table indicates that the stability of MAC tautomers evaluated from the entire energy is in agreement with the temperature dependence of reaction mixture composition previously described. An analysis of the distribution of electron density on the double bond of the isopropenyl group of MAC shows that tautomers *K*, *E*₁-*trans*- and *E*₂ have a direction of electron polarization, typical of monomers with electron donor substituents at the double bond. Electron acceptor properties of the ν -dicarbonyl group are weak and only exist for an *E*₁-*cis* tautomer which is, apparently, due to steric factors resulting in stronger interaction between the carbonyl group of the chelate ring and the double bond of the vinyl group. It should be noted that quantum chemical calculation of *cis*- and *trans*-configurations of the tautomer *K* did not reveal differences in polarization of the double bond of the isopropenyl group.

TABLE 4. PARAMETERS OF COPOLYMERIZATION OF METACROLEIN AND METHYL ISOPROPENYL KETONE

M ₁	M ₂	<i>r</i> ₁	<i>e</i> ₁	<i>r</i> ₂	<i>Q</i> ₁ b	Literatur
MIK (<i>E</i> ₁ - <i>cis</i> model)	VP	4.39	0.01	—	—	*
	St	0.66	0.32	+0.53	1.49	[11]
MA (<i>E</i> ₂ model) (<i>K</i> , <i>E</i> ₁ - <i>trans</i>)	AN	0.70 ± 0.14	0.36 ± 0.08	—	—	[11]
	VP	12.7	0.27	—	—	*
	St	0.88 ± 0.02	0.22 ± 0.02	—0.01	1.76	[12]
	AN	2.0	0.06	—	—	[10]

* *r*₁ and *r*₂ values were calculated from *e* and *Q* values of comonomers.

As shown by Table 3, the energy difference between the energetically most favourable form of *E*₂ and *K* is 15 kcal/mole and between intra-chelate tautomers of *E*₁ and *E*₂— ~3 kcal/mole. In spite of the slight energy difference between tautomers *E*₁ and *E*₂ the kinetic difference of these forms in copolymerization may be significant in view of the fact that their electron structure is different. This is in agreement with results of copolymerization of MAC with various comonomers. A comparison of these results and those of the quantum chemical calculation suggests that the *E*₁-*cis* tautomer is copolymerized mainly with VP and styrene and

E_2 , E_1 -*trans*- and K tautomers, with AN. The degree of electron delocalization ($Q_1 = 5.1$) is very high for the tautomer reacting with AN; bearing in mind that the chain of conjugation of the last three tautomers is the longest for the E_2 tautomer, it is reasonable to assume that it mainly participates in copolymerization with AN.

To understand the behaviour of various MAC tautomers in copolymerization, it was advisable to compare parameters of copolymerization of MAC with VP, St and AN and parameters of several monocarbonyl vinyl monomers with a structure close to the fragment structure at the MAC double bond.

Methylisopropenyl ketone (MIK) and metacrolein (MA) were selected as monomers which in first approximation simulate corresponding tautomers of E_1 -*cis* and E_2 (and also K and E_1 -*trans*).

Constants of copolymerization of model monomers with N-vinylpyrrolidone, styrene and acrylonitrile are shown in Table 4.

A comparison of parameters of copolymerization of MAC and model monomers with VP, St and AN point to some agreement between the kinetic behaviour and electron structure.

Thus, the behaviour of MAC in copolymerization with AN is only simulated by the behaviour of MA—a model of MAC tautomers with electron donor substituents. On the other hand, the behaviour of MAC in copolymerization with comonomers having electron donor substituents is most clearly simulated during copolymerization of MIK with VP and not MA with VP.

A study of parameters of copolymerization of MAC with several vinyl monomers suggests that various MAC tautomers take part simultaneously in copolymerization, however, according to electron distribution on the double bond of the comonomer partner, a given MAC tautomer takes part mainly in the reaction.

Thus, the ability of MAC to undergo tautomeric conversions determined its behaviour during radical polymerization.

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