NUCLEAR MAGNETIC RESONANCE STUDY OF KETO-ENOL TAUTOMERISM IN POLYMERIC 3-DICARBONYL COMPOUNDS

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The introduction of even a small number of β -dicarbonyl units into polyamides [1], cellulose [2], and epoxy resins [3] causes significant changes in their properties. The tautomeric equilibrium of the polymers of this type [4] has not been studied as thoroughly as low-molecular β -dicarbonyl compounds [5-8].

The purpose of the present work was to synthesize polymers with β -dicarbonyl groups in the side chains and to investigate the keto-enol equilibrium in them. The polymeric β -diketone polymethacryloylacetone (PMAC) and the polymeric β -keto ester poly(vinyl acetoacetate) (PVAA) were studied. In order to ascertain the effect of the macromolecular structure on the keto-enol equilibrium, we studied compounds which simulate the elementary unit of the polymers, viz., 2,2-dimethyl-3,5-dione (I) and 1-ethoxybutan-1,3-dione (II).

The tautomeric equilibrium in the systems under study may be represented in the following manner:



In the enol form of PMAC, unlike PVAA, the rapid migration of a proton between the oxygen atoms is possible [5].

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TABLE 1. Chemical Shifts of the Protons δ , ppm (10% solutions in deuteroacetone, 26°, TMS internal standard)

	Protons					
Compound	=CB	-CH2	-0Н			
PMAC (I) PVAA (II)	5,7 5,5 5,1 4,9	$3,7 \\ 3,5 \\ 3,6 \\ 3,4$	16,0 16,1 Washed-out signal 12,0			

Like the low-molecular acyclic β -diketones and β -keto ethers, the enol tautomers of the polymers studied should exist in a chelate form. The report that nonchelate (in particular, trans enol) forms of the cyclic diketones exist in considerable numbers has not been confirmed [6]. In the case of PMAC, this is clearly confirmed by the PMR spectra. The value of the chemical shift of the signal from the OH-group proton in the enol form (Table 1) is typical of the chelate forms [5] and is weakly dependent on the temperature and the solvent (acetone, o-dichlorobenzene, pyridine). The PMR signals of the same protons in nonchelate enols (which have been detected in the case of cyclic diketones and formyl-containing dicarbonyl compounds) are lo-

cated in the range of stronger fields, and their position is strongly dependent on the temperature and the medium [5, 6].

The keto-enol equilibrium of these compounds was studied with the aid of NMR spectroscopy (see Table 1). The concentrations of the keto and enol forms were evaluated, respectively, from the intensities of the signals of the protons in the $-CH_2$ and =CH groups.

The keto-enol equilibrium constants for the various temperatures (Table 2) were evaluated from the formula

$$K = [e]/[\kappa] = 2I_e/I_\kappa$$

where I_e and I_k are the areas of the proton signals for the keto and enol forms.

In PMAC, unlike PVAA, there was a greater degree of enolization than in the corresponding monomer models. The thermodynamic parameters of the keto-enol equilibrium in the polymers and their lowmolecular models were determined from the dependence of log K on 1/T [9] (Fig. 1 and Table 3). In the case of PMAC there were considerable changes in the parameters of the keto-enol equilibrium in the transition from the low-molecular model to the polymer. This seems to be due to the high concentration of the enol forms and the forced proximity between the tautomeric side chains in PMAC. The interactions arising between the tautomeric groups are clearly manifested both in the energy and in the entropy contributions to the free energy of enolization. It may be postulated that besides the formation of intramolecular hydrogen bonds in the side chains of the polymers, the formation of interside-chain hydrogen bonds occurs. These contribute to the higher value of ΔH for PMAC.

The increase in the ΔS value for the polymer may be attributed to the decrease in the conformational freedom of the polymer chain in the transition to the enol form with the rigid chelate rings. This purely polymeric effect is due to a decrease in the number of possible rotamers about the bonds between the atoms of the backbone. There is another contribution to ΔS , which is associated with the "cyclization" of the dicarbonyl chain as a result of enolization, both in the polymer and in the model compound. In addition, the effect of the local dielectric constant (ε) in a solution of the polymer on the relative stability of the tautomeric forms is possible. If the local value of ε in the polymeric random coil is lower than ε in

TABLE 2.	Equilibrium	Constants at	Various	Temperatures
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	т., °С								
Compound	68	-50	-22	14	0	4	y	26	
PMAC (I) PVAA (II)	0,075	0,052	0,045	9,2 0,082	0,038 0,081	5,6	42,5	32,3 5,0 0,033 0,062	

TABLE 2 (continued)

	T., °C								
Compound	43	46	48	50	58	64	66	80	100
PMAC (I) PVAA (II)	0,061	16,2	3,6	0,02	0,054	3,4	10,4	7,1	5,2

Compound	Enthalpy $\Delta H = H_k - H_e$, kcal/	Free energy $\Delta G = G_k - G_e$, kcal/	Entropy $\Delta S = S_k - S_e$, cal/
	mole	mole	mole.deg
PMAC Solution of I Pure liquid [10] PVAA (II)	$\begin{array}{c} 4,8\pm0.5\\ 2,2\pm0.2\\ 3,0\pm0.2\\ 1,0\pm0.3\\ 1,1\pm0.1\end{array}$	$\begin{array}{c} 2,0\pm 0,1\\ 0,98\pm 0,05\\ 1,48\\ -2,1\pm 0,1\\ -1,75\pm 0,03\end{array}$	$\begin{array}{c} 9,0\pm 2,0\\ 4,3\pm 1,0\\ 7,4\pm 0,5\\ 10,4\pm 1,0\\ 9,5\pm 0,5\end{array}$

TABLE 3. Thermodynamic Parameters of the Tautomeric Equilibrium in Deuteroacetone (26°)



Fig. 1. Temperature dependence of the keto-enol equilibrium constants.

acetone, this should stabilize the less-polar cis enol form [5,11]. The foregoing is confirmed by the fact that the ΔH and ΔS values for model (I) in the form of a pure liquid differ less from the ΔH and ΔS values of PMAC than they do in an acetone solution of I.

It has not been ruled out that the tactic nature of the polymer chain can influence the keto-enol equilibrium in PMAC. The stereoregularity of the PMAC sample studied corresponded to 75% syndiotactic diads according to the intensity of the PMR signals of the α methyl backbone groups and the vinyl protons of the enol form, the signals being split into three components corresponding to the inequivalent triad sequences in the polymer chain.

In the case of PVAA the polymer effect is weakly expressed. We attribute this to the small relative concentration of the rigid enol form, the greater flexibility of the keto form of the dicarbonyl sidechain groups of the polymer, and the possibility of the formation of only one type of enol form.

EXPERIMENTAL METHOD

The NMR spectra were recorded on a Jeol C-60-HL spectrometer. The spectra of the polymers and the low-molecular models were recorded in the form of 10% solutions in deuteroacetone. The intensity of the signals was measured both by an electronic integrator and by weighing the areas of the signals. The establishment of the equilibrium concentrations of the tautomers was monitored by repeated recording of the PMR spectrum at a given temperature. The absolute error in the measurement of the concentrations of both forms was 1-2%. The errors in the determination of the equilibrium constant K and the value of ΔS (see Table 2) were evaluated from the variance in three to five measurements. The errors for ΔH and ΔS were evaluated [9] without consideration of the slight error in the measurement of the temperature.

2-Methyl-1-hexene-3,5-dione (Methacryloylacetone). This compound was obtained by condensation of methyl acrylate and acetone in the presence of sodium alkoxide [12,13]. The yield was 20%.

<u>Polymethacryloylacetone</u>. This polymer was obtained by radical polymerization of 2-methyl-1-hexene-3,5-dione [12, 13]. The yield was 95% of the theoretical. The polymer had a characteristic viscosity $[\eta]^{25}$ equal to 0.2 dl/g (CHCl₃).

<u>2,2-Dimethylhexene-3,5-dione</u>. This compound was obtained by condensation of ethyl acetate and 2,2-dimethylbutan-3-one in the presence of metallic sodium. The yield was 17% and the boiling point $65-67^{\circ}$ (29 mm).

<u>Poly(vinyl Acetoacetate)</u>. This polymer was obtained by acylation of polyvinyl alcohol by diketene. A 1-g portion of PVC $([\eta]^{25} 0.3 \text{ dl/g}$ in water) was dissolved in 15 ml of boiling DMFA. The solution was cooled to 60-70°. Three drops of pyridine were added, and 2 g of diketene were introduced dropwise. The reaction was carried out for 2 h. The mass was cooled, and the polymer was precipitated in water. Then the polymer was washed with water, dissolved in acetone, and reprecipitated in ethyl ether. The concentration of residual hydroxyl groups in PVAA was 4% (according to the NMR data).

CONCLUSIONS

1. Carbon-chain polymers with β -diketone and β -keto ester functional groups in the side chains have been synthesized.

2. The tautomeric equilibrium of the polymeric β -dicarbonyl compounds polymethacryloylacetone and poly(vinyl acetoacetate) and low-molecular models of these polymers has been studied. The effect of the macromolecular nature of the polymeric β -diketones on the tautomeric equilibrium is expressed as a significant difference between their thermodynamic equilibrium parameters and those of the low-molecular analog.

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