Synthesis of 2,5-Bis(ethoxycarbonyl)-1,4-cyclohexanedione Derivatives and Investigation of their Tautomerism

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It has been shown that the introduction of tautomerizable units of 2,5-bis(ethoxycarbonyl)-1,4-cyclohexanedione and its amino derivatives into the polymer chain leads to a shift of the tautomeric equilibrium and to the appearance of monoenolic or monoenaminic units.

There are few papers dealing with the synthesis and study of polymers that contain tautomerizable groups. The synthesis of polymers with β-dicarbonyl groups in the side chain by polymerization of methacryloylacetone[1] or its copolymerization with vinyl monomers[2] has been described. It was established by ^{1}H NMR spectroscopy that methacryloylacetone units exist mainly in the enol form.[3]

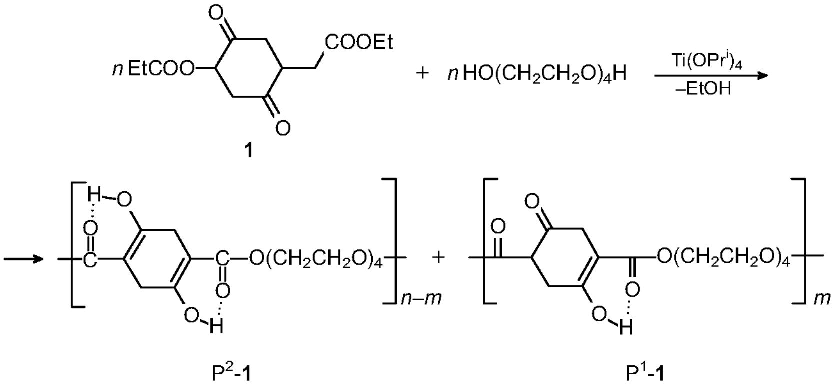
Polymers with β-dicarbonyl groups in the side chain or in the main chain have been obtained by the polymerization of 4-(1,3-pentadienyl)phenyl-4-(6-acryloxyhexyloxy)benzoate[4] or by the polycondensation of 1,3-bis(*p*-hydroxyphenyl)propane-1,3-dione and 4,4-hexamethylenedioxybenzoyl chloride.[5] The synthesis of oligomers containing β-ketone, β-ketoester or β-ketonitrile groups in the chain has also been described.[6,7] The enolization of all these polymers is indicated by their ability to form chelates with transition metal compounds.

Low molecular weight systems capable of undergoing reversible prototropic transformations are being widely investigated. They are of practical interest because tautomeric transformations lead to a change in the properties of the molecular system, *e.g.* its optical and electric properties.[8] On this basis materials for molecular electronics can be obtained. The study of polymer systems is of additional interest because it is possible to control supermolecular organization under the effect of external fields.

In this communication a method for the synthesis of a polymer enol and the products of its chemical transformations is proposed. 2,5-Bis(ethoxycarbonyl)-1,4-cyclohexanedione **1** was used as a β-ketoester monomer. It was synthesized by diethylsuccinate condensation according to Dickman[9] and exists in solution and in the condensed state completely in the form of dienol.[10,11]

The polymers were synthesized by the polycondensation of **1** and tetraethylene glycol which was carried out by transesterification because the preparation of a free diacid is complicated by decarboxylation reactions.[12,13] Decarboxylation of **1** readily proceeds at high temperatures in the presence of acid catalysts.[9] Therefore, transesterification was carried out in the melt in an argon flow by increasing the temperature stepwise from 140 °C at the start of polycondensation to 185 °C at its completion in the evacuation stage (Scheme 1).†

p-Toluenesulfonic acid, sulfocation exchanger KU-2 (Russia), or Ti(OPr^i)$_4$ were used as transesterification catalysts. It was found that in the presence of *p*-toluenesulfonic acid below 140 °C oil-like oligomers are formed. When the temperature is increased to 170 °C, cross-linked products are obtained. This is probably the result of cross-linking



Scheme 1 *Conditions*: temperature, °C (time, h): 140 (1), 150 (1), 160 (1), 175 (0.5), 185 (0.5), 185/1 mmHg (0.5). **P-1** was precipitated from MeOH and re-precipitated from CHCl$_3$ in MeOH. **P-1** has [η] 0.25 dl g^{-1} (CHCl$_3$, 25 °C).

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† *Analytical characteristics.* IR spectra were measured on a Bruker IFS 88 spectrometer in CHCl$_3$ or in the condensed state; ^{1}H NMR spectra were measured on a Bruker AC 200 spectrometer in CDCl$_3$; UV spectra were measured on a Specord M 40 in EtOH.

1: m.p. 130 °C (from EtOH); UV λ_{max}/nm 241; IR ν/cm^{-1} 1661 (C=O in chelate), 1622 (C=C in ring); ^{1}H NMR (δ/ppm) 12.17 (HO in dienol).

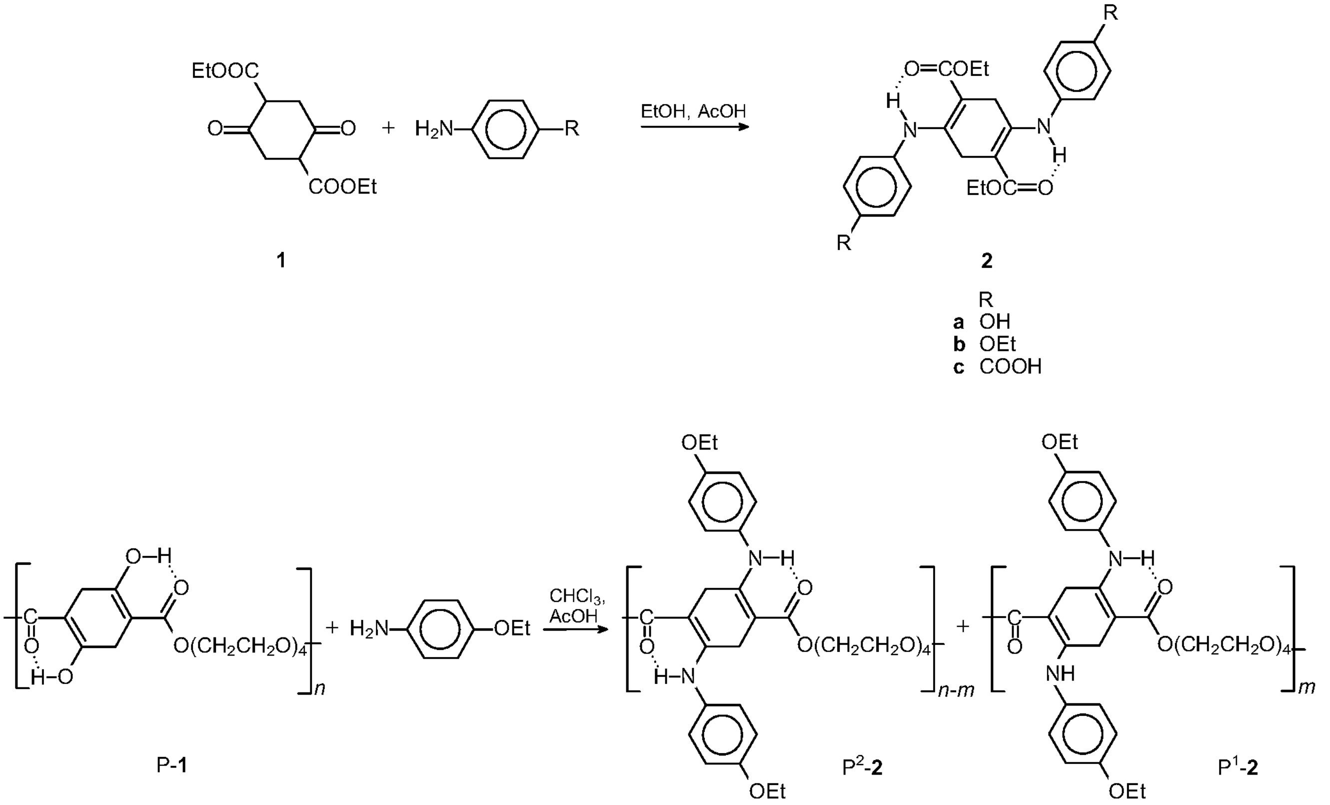
2a: m.p. 218 °C (decomp., from DMF); %N (found/theor.) 6.29/6.39; UV λ_{max}/nm 222, 306, 440; IR ν/cm^{-1} (cryst.) 1672 (C=O in chelate), 1641 (C=C in ring).

2b: 237 °C (decomp., from DMF); %N (found/theor.) 4.57/4.70; UV λ_{max}/nm 242, 331; IR ν/cm^{-1} (cryst.) 1673 (C=O in COOH), 1641 (C=O in chelate), 1600 (C=C in ring).

P-1: m.p. 69–71 °C; IR ν/cm^{-1} 1736 (C=O in non-chelate ester groups), 1664 (C=O in chelate), 1625 (C=C in ring); ^{1}H NMR (δ/ppm) 12.17 and 12.06 (HO of di- and monoenolic groups in the inner units of the polymer), 10.15 and 9.98 (HO of di- and monoenolic groups in the terminal units), 7.28 (H in COOH).

P-2: m.p. 76–78 °C; %N (found/theor.) 4.61/4.76; IR ν/cm^{-1} 1686 (C=O in non-chelate ester groups), 1651 (C=O in chelate), 1599 (C=C in ring); ^{1}H NMR (δ/ppm) 10.4 and 10.3 (HN of di- and monoenaminoketone groups in the inner units), 7.78 (HN of dienaminoketone groups in the terminal units).

P-3: m.p. 65–67 °C; %N (found/theor.) 4.84/4.76; IR ν/cm^{-1} 1756 (C=O in non-chelate ester groups in the polymer), 1728 (C=O in non-chelate ester groups in the substituent), 1653 (C=O in chelate), 1599 (C=C in ring); ^{1}H NMR (δ/ppm) 11.08 and 10.95 (HN of di- and monoenaminoketone groups in the inner units), series of double signals in the region of 8–10 (HN groups which are removed from differing distances from the end of the chain).



Scheme 2 Synthesis of **2a–c** or P-**2**: boiling **1** or P-**1** and aromatic amines in argon flow. P-**2** has [η] 0.26 dl g^{-1} ($CHCl_3$, 25 °C).

reactions proceeding with the participation of the OH enol groups. The use of a KU-2 cation exchanger at these temperatures does not lead to polymer synthesis. The optimum results were obtained with a typical transesterification catalyst $Ti(OPr^i)_4$ in the presence of which polyesters in 80–90% yield with an [η] value of 0.20–0.28 dl g^{-1} were prepared.

The polymers were characterized with the aid of IR and ^{1}H NMR spectra. It follows from the P-1 region of the IR spectrum assigned to groups taking part in prototropic transformations that the absorption bands at 1664 and 1625 cm^{-1} (C=O and C=C) analogous to bands for **1** at 1661 and 1622 cm^{-1} can be assigned to the units in the chelate keto-enol form with intramolecular hydrogen bonds, whereas the absorption band at 1736 cm^{-1} characteristic of C=O in the non-chelate ester group shows that di- and monoenol units, P^2-**1** and P^1-**1**, coexist in P-**1**.

Since the molecular weight of P-**1** is low, its ^{1}H NMR spectra are of a complex character because they actually consist of two sub-spectra corresponding to inner and terminal chain fragments. The enol OH groups of the inner units exhibit signals at 12.06 and 12.17 ppm which are assigned to di- and monoenols and have an intensity ratio of ~10:1, whereas the corresponding end fragments exhibit signals at 9.98 and 10.15 ppm (their intensity ratio is ~6:1). If follows from the ratio of total signal intensities of internal and total protons which is equal to ~8:1, that the degree of polymerization of P-**1** is ~10 and the mean content of enol protons is 1.9 per unit. Moreover, the spectra of P-**1** exhibit weak signals at 7.28 ppm assigned to the protons of the COOH group in the end unit. Their appearance may be explained by secondary reactions of chain termination under polycondensation conditions. The intensities of NMR signals of carboxylic groups and enol groups in the end units are about equal.

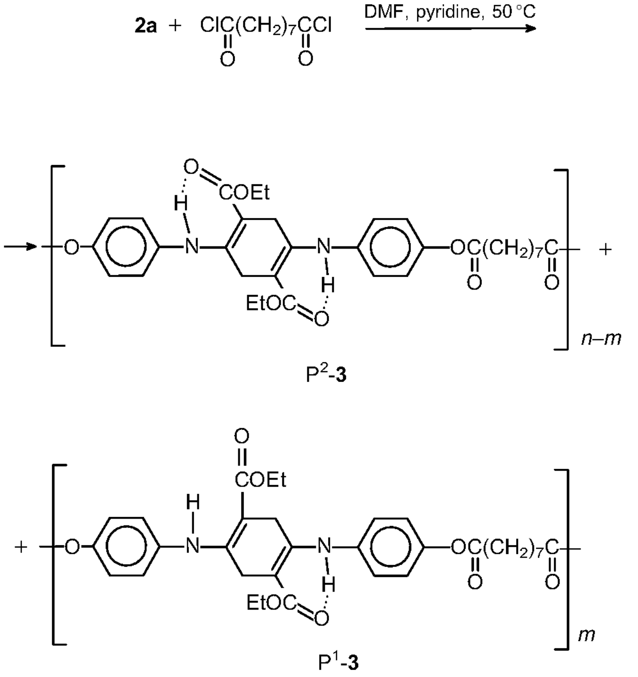
P-**1** contains in each inner unit two tautomeric ketoester groups and a ketoacid group in the end unit which in the interaction with primary amines are known to form β-aminovinylketones capable of tautomerization in quantitative yield.[14] The reactions of interaction between **1** and some amines have already been described.[15,16] The synthesis of compounds which have not yet been described was carried out by a published method[15] (Scheme 2). Furthermore, P-**3** was synthesized on the basis of diphenol **2a** (Scheme 3).

The absence in the IR spectra of **2a–c** of absorption bands in the regions of 1700–1760 cm^{-1} typical of unperturbed ester (1725–1760 cm^{-1}) or COOH (1690–1710 cm^{-1}) groups and the presence of C=O absorption bands in ketoenamine at 1672, 1655 and 1641 cm^{-1} (for **2a–c**, respectively) as well as that of absorption of the endocyclic C=C bond at 1641, 1615 and 1600 cm^{-1} prove that **2a–c** exist in the form of enaminoketones. Moreover, the spectrum of **2c** exhibits a band at 1673 cm^{-1} (COOH). Its marked shift towards low frequencies may be due to the effect of the aminated cyclodiene central unit in the molecule of **2c**.

P-**2** and P-**3** also exist predominantly in the form of enediaminoketones which follows from their IR spectra: according to refs. 17 and 18, the bands at 1651 and 1653 cm^{-1} should be assigned to C=O absorption in enediamine P^2-**2** and P^2-**3** units, whereas the absorption at 1610 and 1599 cm^{-1} is assigned to the endocyclic C=C bond. However, P-**2** and P-**3** exhibit absorption bands at 1686 and 1728 cm^{-1} assigned to the unperturbed C=O in the ester groups and indicating that enaminoaminoketones are present in these polymers.

For P-**3** at 1756 cm^{-1} an additional C=O absorption of the intra-chain ester group is observed.

The ^{1}H NMR spectra of P-**2** and P-**3** also consist of two sub-spectra and contain the signals of the NH groups of enaminoaminoketones at 10.4 and 11.06 ppm (P-**2** and P-**3**, respectively). The intensity of these signals is much lower than that of signals at 10.3 and 10.95 ppm which correspond



Scheme 3 P-**3** was precipitated from MeOH and re-precipitated from DMF in MeOH. P-**3** has [η] 0.37 dl g^{-1} (DMF, 25 °C).

to the protons of NH groups in enediaminoketones, *i.e.* P^2-**2** and P^2-**3**.

It may be concluded from these results that the insertion into the polymer chain of fragments existing in the monomer form as dienols or enediaminoketones leads to a shift in the tautomeric equilibrium and to the appearance of considerable quantities of monoenol (in the case of P-**1**) and enaminoketone (in the case of P-**2** and P-**3**) tautomers. This polymeric effect may be associated with a decrease in the chain entropy because of a smaller set of rotational isomers in the main chain.

It was shown that all these polymers form coloured insoluble complexes with salts of transition metals. The study of prototropic transformations and complexations is to be continued.

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