On the Synthesis of Ethyl-2-Cyanoacrylate from Waste Residue

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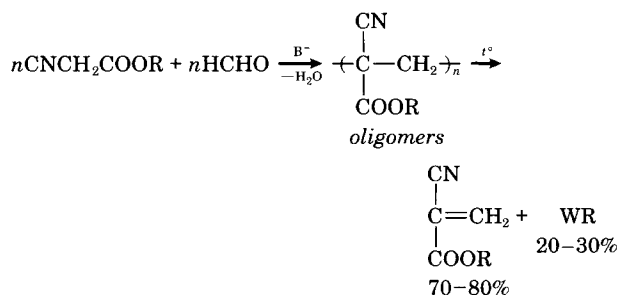Scientific-Research Centre for Speciality Polymers, 4A Kliment Ochridsky Str., 1756-Sofia, Bulgaria

SYNOPSIS

The aim of the present study is to clarify some problems concerning the synthesis of additional quantities of ethyl-2-cyanoacrylate monomer (ECA) utilizing the waste residue (WR) from the large-scale depolymerization of ECA oligomers. The composition of WR was established by GPC and IR spectroscopy. WR was found to consist mostly of diethyl dicyanoglutarate (DEDCG) and low molecular weight products of its condensation with paraformaldehyde (pFA). The DEDCG–pFA interaction was studied as a model, and the influence of DEDCG conversion on the average degree of polymerization ($\bar{x}_n$ and $\bar{x}_w$) of the oligomers formed was also followed. On this basis, it was found that oligomer formation in condensation of WR with pFA is consistent with a stepgrowth mechanism, the polymer chain length being determined by steric hindrance and destructive reactions.

INTRODUCTION

Alkyl-2-cyanoacrylates are well known as instant adhesives useful in bonding operations involving a variety of substrates. Most frequently, the industrial synthetic routes to their production are based on a two-stage reaction scheme proposed for the first time by Ardis[1] comprising
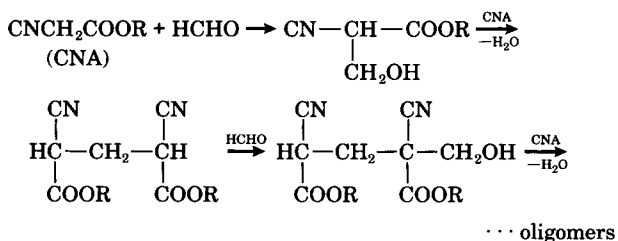
  i. base-catalyzed condensation of alkyl cyanoacetates with formaldehyde to form low molecular weight polymers; and

  ii. subsequent vacuum depolymerization of the condensation oligomers to get monomeric 2-cyanoacrylates (up to 80% of theory):
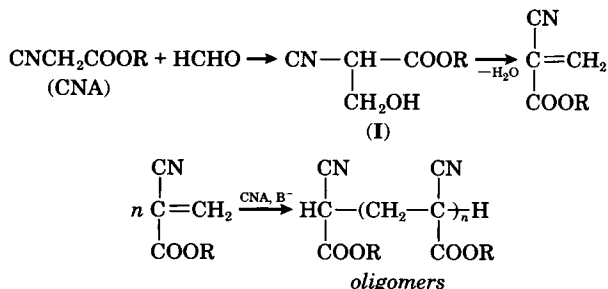
$$n\,CNCH_2COOR + n\,HCHO \xrightarrow[-H_2O]{B^-} \left(\begin{array}{c} CN \\ | \\ C-CH_2 \\ | \\ COOR \end{array}\right)_n \xrightarrow{t^\circ}$$

oligomers

$$\begin{array}{c} CN \\ | \\ C=CH_2 \\ | \\ COOR \\ 70-80\% \end{array} + \begin{array}{c} WR \\ 20-30\% \end{array}$$

wherein R = alkyl and B^- = organic or inorganic base.

The waste residue is a brownish-to-black product. No data of its composition and structure were found in the literature.

Early studies attributed the polymer formation in the first stage to a stepwise condensation of the type[2,3]

$$CNCH_2COOR + HCHO \rightarrow \begin{array}{c} CN-CH-COOR \\ | \\ CH_2OH \end{array} \xrightarrow[-H_2O]{CNA}$$

(CNA)

$$\begin{array}{c} CN \\ | \\ HC-CH_2-CH \\ | \quad\quad | \\ COOR \quad COOR \end{array} \xrightarrow{HCHO} \begin{array}{c} CN \quad\quad CN \\ | \quad\quad\quad | \\ HC-CH_2-C-CH_2OH \\ | \quad\quad\quad | \\ COOR \quad COOR \end{array} \xrightarrow[-H_2O]{CNA}$$

··· oligomers

This condensation mechanism, however, was not confirmed in subsequent communications. A kinetics study carried out by Rooney[4] yielded evidence that the oligomer formation in the ethyl cyanoacetate (ECAc)/paraformaldehyde (pFA) interaction should be attributed to an anionic polymerization process; the following reaction scheme was proposed that included a stage of cyanoacrylate separation:

$$CNCH_2COOR + HCHO \rightarrow \begin{array}{c} CN-CH-COOR \\ | \\ CH_2OH \end{array} \xrightarrow[-H_2O]{} \begin{array}{c} CN \\ | \\ C=CH_2 \\ | \\ COOR \end{array}$$

(CNA)   (I)

$$n\begin{array}{c} CN \\ | \\ C=CH_2 \\ | \\ COOR \end{array} \xrightarrow{CNA,\,B^-} \begin{array}{c} CN \quad\quad\quad CN \\ | \quad\quad\quad\quad | \\ HC-(CH_2-C)_n-H \\ | \quad\quad\quad\quad | \\ COOR \quad\quad COOR \end{array}$$

oligomers

where R = ethyl; B⁻ = organic or inorganic base; and n = 5–10.

Under the basic conditions, the cyanoacrylate monomer generated after the intramolecular dehydration of the methylol compound (I) polymerizes rapidly. The low observed molecular weight of the oligomers was said to be due to a chain transfer to the ECAc molecules.[5]

Recently, it has been established that a pretreated WR can be used instead of ECAc in the stage of condensation with pFA, thus also yielding oligomer products. Additional amounts of monomeric ethyl-2-cyanoacrylate (ECA) have been produced by subjecting the said oligomers to a vacuum depolymerization.[6]

The purpose of this work was to discuss all questions concerning the use of WR as a starting material for ECA synthesis. Experiments were carried out to determine the composition of waste residue (WR) and the regularities of its interaction with pFA. An attempt is also made to clarify the mechanism of oligomer formation in this particular case.

EXPERIMENTAL

Before using it for the purpose of the present study, WR was subjected to a treatment according to Ref. 6—dissolution in toluene, washing, and neutralization of the organic solution. Subsequently, WR was reacted with pFA in glass or stainless-steel vessels fitted with a mechanical stirrer, thermometer, and Dean–Stark reflux trap. A typical reaction charge included (weight parts): WR, 100; toluene, 120; and piperidine, 0.20, the amounts of pFA being varied in the range of 1–8 wt parts. In this way, different condensation oligomers were synthesized. During the reactions, the temperature was increased gradually from 82 to 110°C. After the entire separation of the reaction water, samples from the reaction mixture were removed and neutralized with acetone solution of methanesulfonic acid. The oligomers were isolated by evaporation of the solvents under low pressure. Their molecular weights were determined on tetrahydrofuran solutions in a Waters-II M 440 gel permeation chromatograph equipped with Ultrastyragel columns (2 × 100 Å and 1 × 500 Å). Oligomers produced from WR with various amounts of pFA were afterward subjected to depolymerization, conducted in the presence of a catalytic system containing P_2O_5 and hydroquinone, at 150–180°C/10 mmHg, thus yielding different quantities of ECA.

The necessary α,α'-diethyl dicyanoglutarate was prepared by reacting pFA with ECAc in the mol ratio 1 : 4. This reaction was performed in toluene azeotropically removing the reaction water. Piperidine 0.1 wt %, was applied as a catalyst. The diethyl dicyanoglutarate (DEDCG) produced was isolated by fractionating vacuum distillation in an inert atmosphere at 130–132°C/0.1 mmHg. This compound was used both to calibrate the chromatograph and to investigate its interaction with pFA. In the last case, a series of condensations were carried out in a reactor analogous to that previously described. Each charge included 0.25 mol (60 g) DEDCG; 0.25 mol (7.73 g) pFA; 0.05 cm³ piperidine, and 50 cm³ toluene. The reactions were conducted at 85–110°C to different degrees of DEDCG conversion, which were estimated on the basis of water evolved from the condensation that was noted and used to compute the percentage conversion of the DEDCG. Oligomer samples were prepared and studied by GPC as mentioned above.

To prove the hydroxyl-containing intermediate compound in the pFA–DEDCG interaction, condensations were carried out, taking the reactants in a mol ratio 4 : 1 in favor of pFA. Thus, 0.12 mol pFA was stirred, while heating at 80°C, in 30 cm³ benzene. At the same time, a solution of 0.03 mol DEDCG and catalytic amounts of piperidine in 30 cm³ benzene was added dropwise over a period of 2 h, intensively stirring and refluxing the reaction mixture. The latter was cooled to room temperature and the solvent was decanted. To obtain a solution that was filtered to remove the pFA excess, 50 cm³ of acetone were added instead of benzene. After a drying procedure with anhydrous Na_2SO_4, the drying agent and the acetone were taken off. The product obtained by this procedure had a moisture content of less than 0.1% (Karl Fischer titration).

To get structural confirmation of the GPC data, IR spectroscopy was involved. All IR spectra were recorded on a Specord-M80 apparatus in $CHCl_3$ solutions.

RESULTS AND DISCUSSION

Figure 1 depicts a gel-permeation chromatogram of unreacted WR. Clearly defined peaks of low molecular weight products were detected. Samples of DEDCG and ECAc were also chromatographed. The data obtained were used to calibrate the system. For that purpose, a semilogarithmic plot of molecular weights as a function of the retention time was constructed, as shown in Figure 2.

From the IR spectra comparison of DEDCG [Fig. 3(A)] and WR [Fig. 3(B)], it is evident that an
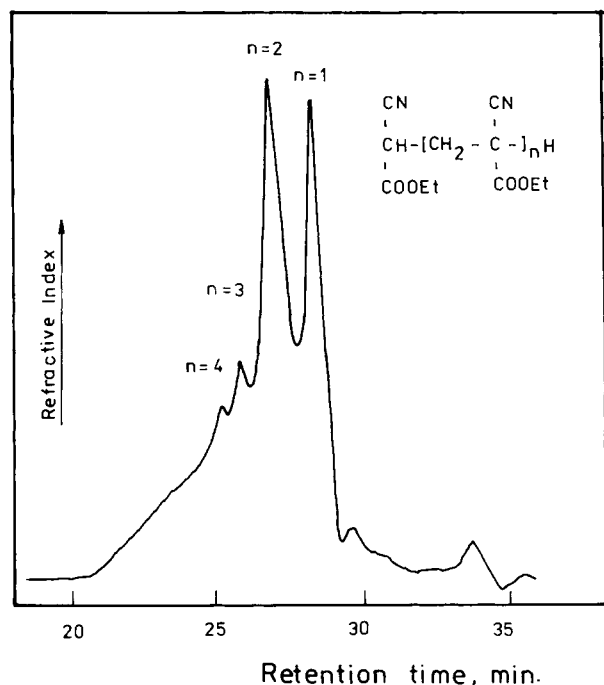
Figure 1   Gel-permeation chromatogram of unreacted WR; GPC conditions: tetrahydrofuran solvent at 45°C and flow rate 1.0 mL/min; Ultrastyragel columns: 2 × 100 Å and 1 × 500 Å.

analogous molecular structure of these two samples should be supposed. Therefore, taking into account the above-noted GPC data, we came to the conclusion that WR is to be considered as a mixture of DEDCG structural homologs of the following general formula:

$$
\begin{array}{cc}
\text{CN} & \text{CN} \\
| & | \\
\text{CH}-(\text{CH}_2-\text{C}-)_n\text{H} \\
| & | \\
\text{COOR} & \text{COOR}
\end{array}
$$
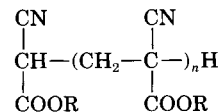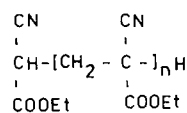
where R = ethyl and $n = 1, 2, 3, \ldots$

From Figure 1 it is also evident that DEDCG ($n = 1$) and the product with $n = 2$ are the main components of WR. Hence, these components should mostly take part in the condensation with pFA.

There is a good correspondence between the last statement and the GPC data shown in Figure 4. It can be seen that during the WR-pFA condensation it is DEDCG that reacts at first, and only afterward, does the next homolog with $n = 2$ enter into the reaction. An almost complete exhaustion of the latter occurs at a WR : pFA ratio of 100 : 5. As a result, the average molecular weight of the oligomers rises considerably. An analogous trend is evident at a further increase (up to 8 wt %) of pFA concentration. At the same time, however, well-distinguished peaks corresponding to a molecular weight in the range of 150–160 appeared in the chromatograms.

In Table I, data for M_w, M_n, and their ratios are tabulated for the same polymers. For comparison, the reaction times required to complete the condensation entirely are shown in this table.

The pFA concentration exerts a considerable influence upon the molecular weights of the oligomers—The bigger the pFA amounts in the starting mixture, the higher the oligomer molecular weights. Although only slightly, the polydispersity also rises. A similar behavior is typical to a great number of polycondensation processes.
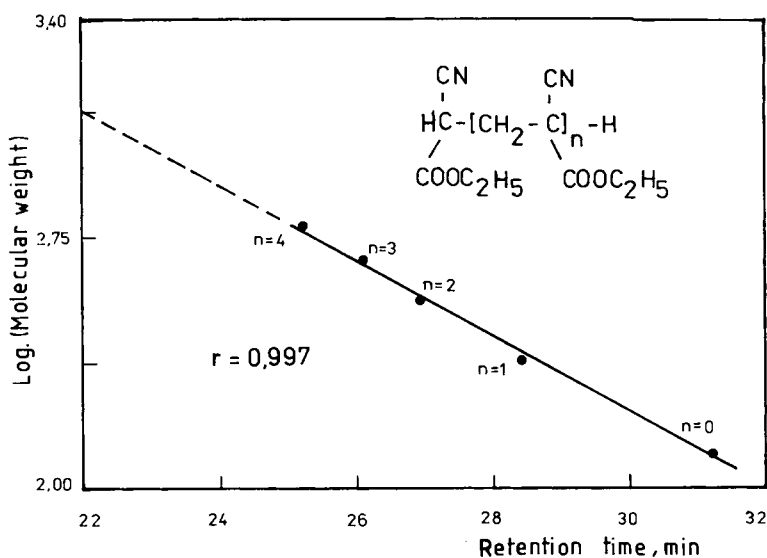

Figure 2   GPC calibration plot for ethyl cyanoacrylate oligomers derived from Figure 1.
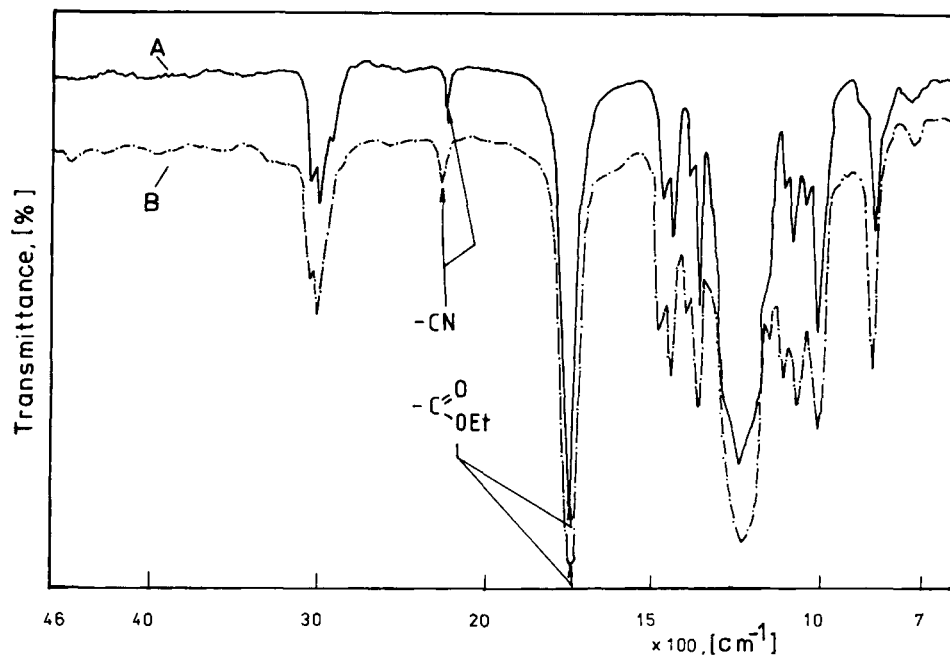
Figure 3 IR spectra of (A) DEDCG and (B) WR. $CHCl_3$ solution.

From Table I is also evident that at pFA concentrations above 5 wt % a substantial increase of the necessary reaction time was registered. This effect is in good agreement with the presence of low molecular weight products (see Fig. 4) that are attributed to destructive reactions. These undesirable side processes were more likely to happen when both the

Figure 4 Influence of pFA content on the molecular weight distribution of oligomer samples prepared by the WR–pFA reaction.

duration and the average molecular weights increased.

Each of the condensation oligomers produced from WR with definite quantities of pFA was pyrolyzed in vacuum in a manner described above. That allowed the evaluation of the influence of oligomer molecular weight upon the yields of purified ECA. The relationship shown in Figure 5 was found to have a well-expressed maximum.

It is of practical interest to explain the nature of oligomer formation in the WR–pFA reaction. There are no data and no studies on this matter. The problem is complicated in view of the fact that WR was found to be a mixture but not a defined compound.

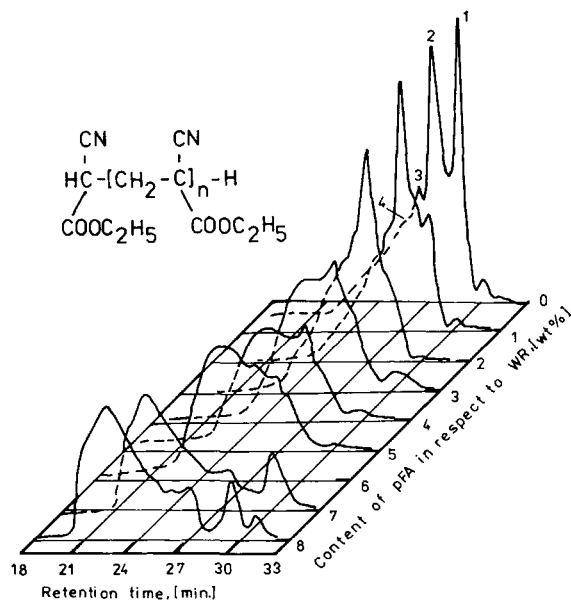Leaving out possible side reactions, we presumed

Table I Effect of Weight Ratio pFA : WR on the Oligomer Molecular Weights

Weight Ratio pFA : WR	Condensation Time (min)[a]	M_n	M_w	M_w/M_n
0/100	—	272	350	1.29
1/100	90	286	400	1.40
2/100	90	340	456	1.34
3/100	90	354	481	1.36
4/100	90	355	530	1.49
5/100	90	395	600	1.52
7/100	110	434	683	1.57
8/100	130	450	720	1.60

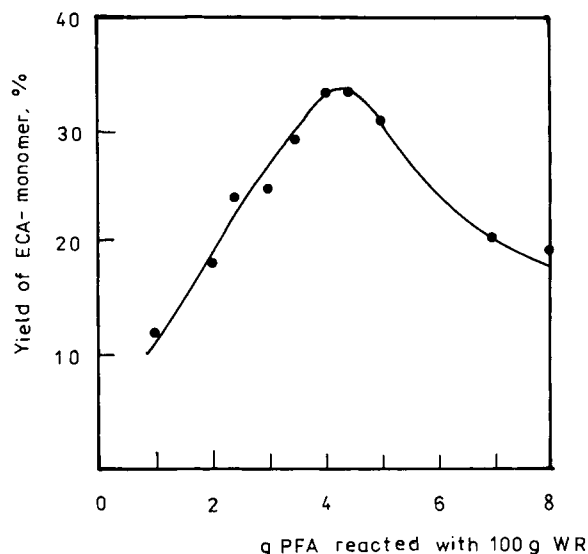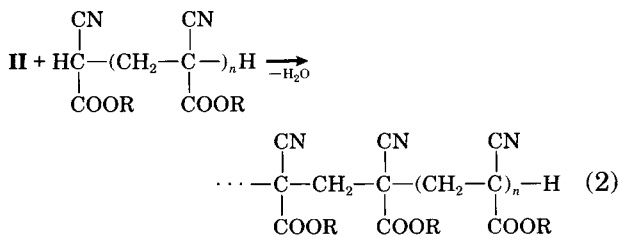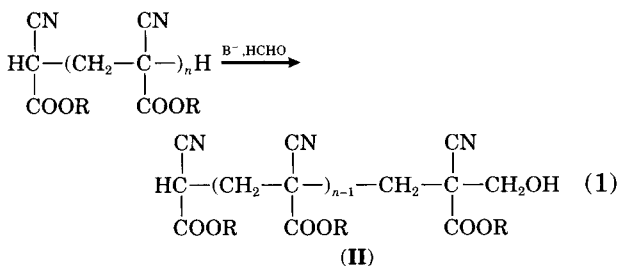[a] Measured after entire removal of the reaction water.

Figure 5 Influence of pFA concentration in the pFA–WR reaction on the yields of purified ECA monomer obtained after depolymerization of condensation oligomers.
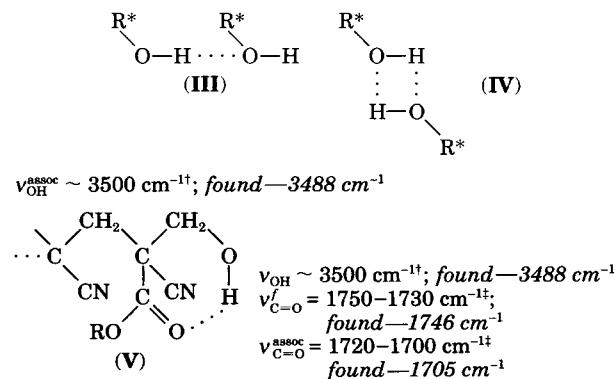
that with some approximations the WR–pFA reaction can be considered as a ordinary stepwise condensation. As a rule, such processes are completed between functional groups already existing in the starting monomers. In the studied case, however, the polymer chain propagation requires, at first, creation of OH groups bonded to the primary carbon atom in the DEDCG homologs. These groups could react afterward with activated H-atoms of another molecule:

$$\underset{\underset{COOR}{\overset{CN}{|}}}{HC}-(CH_2-\underset{\underset{COOR}{\overset{CN}{|}}}{C}-)_nH \xrightarrow{B^-,HCHO}$$

$$\underset{\underset{COOR}{\overset{CN}{|}}}{HC}-(CH_2-\underset{\underset{COOR}{\overset{CN}{|}}}{C}-)_{n-1}-CH_2-\underset{\underset{COOR}{\overset{CN}{|}}}{C}-CH_2OH \quad (1)$$

$$(\mathbf{II})$$

$$\mathbf{II} + \underset{\underset{COOR}{\overset{CN}{|}}}{HC}-(CH_2-\underset{\underset{COOR}{\overset{CN}{|}}}{C}-)_nH \xrightarrow{-H_2O}$$

$$\cdots-\underset{\underset{COOR}{\overset{CN}{|}}}{C}-CH_2-\underset{\underset{COOR}{\overset{CN}{|}}}{C}-(CH_2-\underset{\underset{COOR}{\overset{CN}{|}}}{C})_n-H \quad (2)$$

According to the scheme above the stage of intramolecular dehydration of the methylol compound (**II**) to give free cyanoacrylate monomer would be

impossible in the present case. This is due to the absence of a H-atom in the α-position to the carbon atom bearing the OH group. Therefore, an intermolecular dehydration could be predicted, thereby accepting a step-growth chain propagation mechanism.

To produce evidence in support of this mechanism, it was essential, first of all, to prove the formation of the methylol compound (**II**) that will be an unavoidable intermediate product if a stepwise condensation takes place as we supposed. For that purpose, we studied the DEDCG–pFA reaction by means of IR spectroscopy. Based on general considerations, we expected that the hydroxyl derivative of DEDCG, once formed, would react immediately to give oligomers according to eq. (2) if the DEDCG–pFA ratio were near to the equimolar. That is why the reactants were taken in a mol ratio 4 : 1 in favor of pFA, so as to stop their interaction at the first stage [eq. (1)]. This reaction was performed as previously described. The product that was found to be insoluble in benzene was carefully dried. Its IR spectrum in $CHCl_3$ was recorded in the 3800–2000 cm^{-1} and 2000–1600 cm^{-1} range in concentrations of $1.5 \cdot 10^{-2}$ mol/L and $0.8 \cdot 10^{-2}$ mol/L, respectively [Fig. 6(B)]. Under the same conditions, the spectrum of the starting DEDCG was also obtained [Fig. 6(A)]. A massive absorption peak was detected in spectrum B corresponding to the stretching vibrations. (ν_{OH}^{assoc}) of associated OH groups. That was recognized as a structural confirmation of the hydroxyl-containing intermediate product. The absence of IR absorption in the 3620–3600 cm^{-1} range for free OH groups and the characteristic splitting of the ester carbonyl band in spectrum B allowed the supposition of self-association effects to form dimers (**III**) and (**IV**) as well as intramolecular H-bond formation of the type—OH $\cdots$ O$=$C (**V**):

$$\underset{(\mathbf{III})}{\overset{R^*}{\underset{O-H\cdots O-H}{\diagdown}}} \qquad \underset{\underset{\underset{R^*}{\diagup}}{H-O}}{\overset{R^*}{\underset{\vdots \quad \vdots}{\underset{O-H}{\diagdown}}}} \quad (\mathbf{IV})$$

$\nu_{OH}^{assoc} \sim 3500$ $cm^{-1\dagger}$; *found—3488 cm^{-1}*

$\nu_{OH} \sim 3500$ $cm^{-1\dagger}$; *found—3488 cm^{-1}*
$\nu_{C=O}^f = 1750–1730$ $cm^{-1\ddagger}$;
found—1746 cm^{-1}
$\nu_{C=O}^{assoc} = 1720–1700$ $cm^{-1\ddagger}$
found—1705 cm^{-1}

R* = DEDCG moiety.
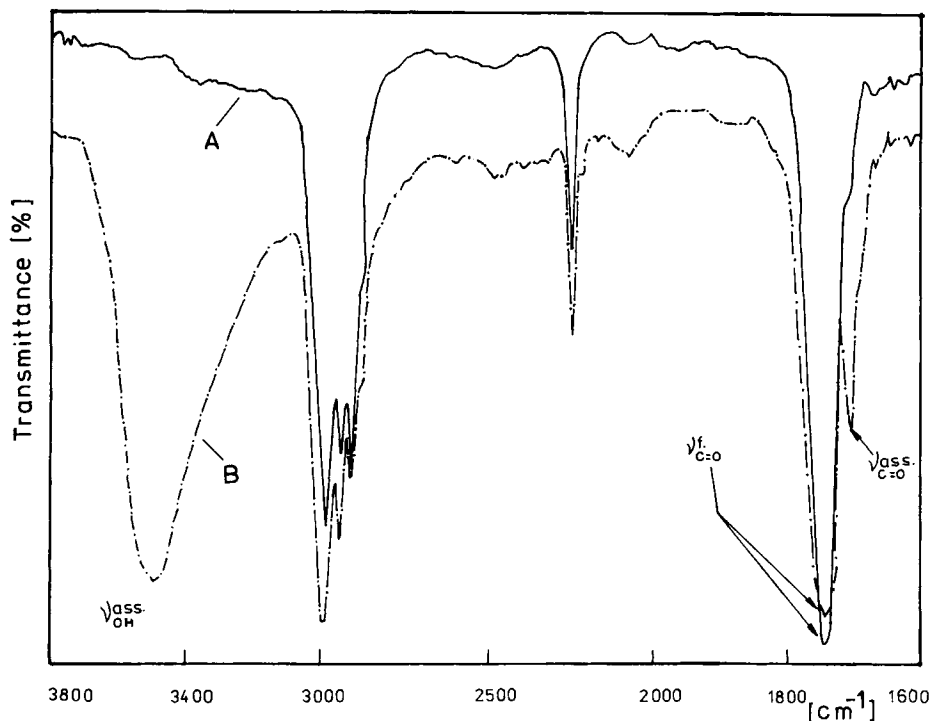† According to Ref. 7.
‡ According to Ref. 8.

Figure 6 IR spectra of (A) DEDCG and (B) reaction product obtained by reacting pFA with DEDCG in the mol ratio 4 : 1. $CHCl_3$ solutions.

More evidence in favor of the step-growth condensation mechanism was obtained when the kinetics of the pFA–DEDCG reaction was followed. Having in mind that DEDCG is to be considered as a bifunctional monomer, and pFA, as a monofunctional one, in the case when they react in equimolar ratio, the following equations for calculating the average degree of polymerization ($\bar{x}_n$ and $\bar{n}_w$) can be applied[9]:

$$\bar{x}_n = \frac{1}{1 - p \cdot (r)^{0.5}} \qquad (3)$$

$$\bar{x}_w = \frac{1 + p \cdot (r)^{0.5}}{1 - p \cdot (r)^{0.5}} \qquad (4)$$

Here p is the degree of polycondensation completion calculated on the basis of evolved water amounts and r is the stoichiometric debalance in the system that in the present case is equal to 0.5.

In Figure 7 theoretical curves (dashed lines) describing the correlations $\bar{x}_n = f(p)$ and $\bar{x}_w = f(p)$ derived from eqs. (3) and (4) are given. In the same plot, the values of $\bar{x}_n$ and $\bar{x}_w$ found from GPC data

of oligomer samples withdrawn from condensations of pFA with DEDCG in toluene are also shown as a function of DEDCG conversion. The data indicated a very good agreement between the theoretical and practically determined results for $\bar{x}_n$ and $\bar{x}_w$. The deviations from the theoretical course of the curves
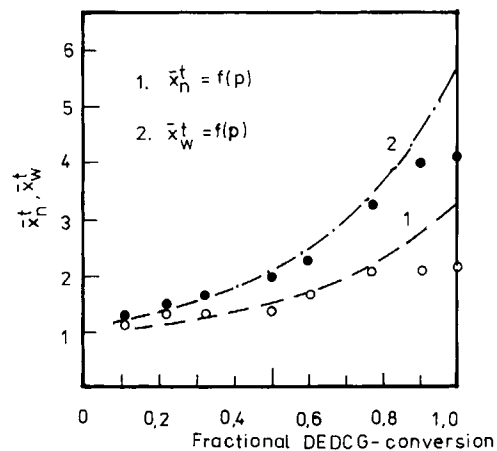

Figure 7 Average degree of polymerization vs. DEDCG conversion during DEDCG–pFA condensation.

when $P \geqslant .8$ could be explained in terms of steric hindrance effects and with destructive reactions analogous to those established in the WR–pFA interaction.

CONCLUSIONS

The data obtained indicate that unlike the ECAc–pFA interaction the oligomer formation in WR–pFA condensation may be attributed to a step-growth process. The average molecular weight of the oligomers, i.e., the polymer chain length, was found to be governed by the WR–pFA ratio and to be limited by steric hindrance and destructive reactions occurring at a higher degree of condensation completion.

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