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Polymerization of itaconic acid

Summary — Poly(itaconic acid) (PIA) has been prepared by various methods namely in radical polymerization in the presence of various initiators and using water or dioxane as reaction medium, or by poly(itaconic anhydride) hydrolysis. The main purpose was to investigate the effect of method of synthesis on the chemical structure of the product. Possibilities of the structures described by Formula (II) or (III) occurring have been considered. The following methods were used for PIA characterization: FT-IR, ¹H NMR, ¹³C NMR, elemental analysis, size exclusion chromatography and conductometric titration as well as potentiometric titration. The reasons of known phenomenon of limited availability of PIA carboxylic groups in titration conditions were discussed. Significant effect of drying conditions on the results obtained suggests the importance of keeping the drying conditions constant. Two types of neighborhood of methylene or carboxylic groups in PIA have been found.

Key words: itaconic acid, polymerization, poly(itaconic acid), chemical structure.

According to the literature [1, 2] the radical homopolymerization of itaconic acid (IA) (Formula I) leads to a product of complicated structure. Marvel and Shepherd [1] have found that the polymerization of IA in 0.5 M HCl initiated by potassium persulphate at 50 °C results in poly(itaconic acid) (PIA), but the process takes



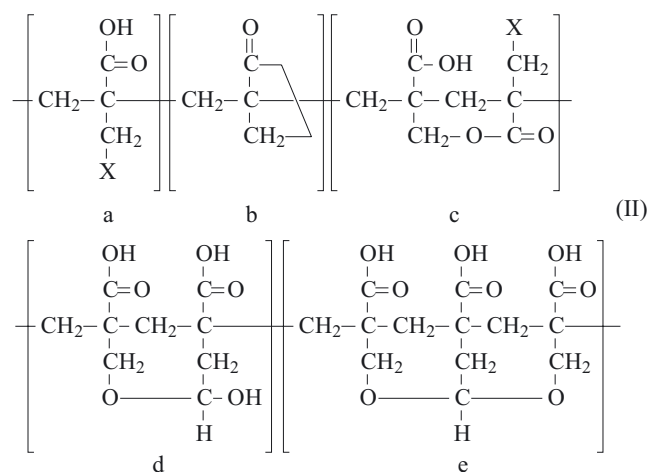
quite a long time. According to the authors the product is hydrated by one molecule of water per one unit and when it is dried over phosphorus pentoxide at 100 °C and under 1 mm Hg (*i.e.* 133 Pa) pressure, this treatment results in the formation of anhydride to an extent of about 30 %.

Braun and El Sayed [2] have examined more deeply the structure of the product of IA polymerization in a dioxan solution. The authors used benzoyl peroxide or 2,2'-azobisisobutyronitrile (AIBN) as an initiator. However, in all cases the process of IA polymerization took a very long time, up to 720 hours.

Performing potentiometric titration of the products obtained, the authors [2] have found that the polymers contain only a half of the acid groups of a hypothetical PIA. They suggest the formation of anhydride groups, following decarboxylation and propose a schema of reaction based on a set of chain transfer reactions.

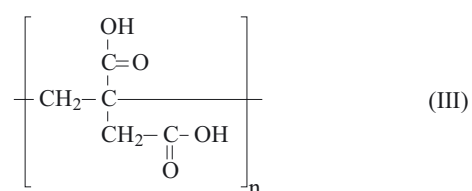
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In accordance with this process, the authors [2] suggest that the following groups may be formed:



where: X = -OH or -CHO

In order to obtain poly(itaconic acid) with the following structure:



Yokota and co-workers [3] have proposed a new method of synthesis. In its first step, poly(itaconic anhydride) is obtained by polymerization of itaconic anhydride, and then after hydrolysis one can obtain poly(itaconic acid) with two carboxylic groups in a single polymer unit. The structure of PIA has been confirmed by elemental analysis with the assumption that each polymer unit is hydrated by one molecule of water experimental: C 39.89—41.19 %, H 5.11—5.30 %; theoretical for poly(IA · H₂O): C 40.54 %, H 5.55 %. However, the authors have not confirmed the amount of carboxylic groups by titration.

More recently [4], it has been reported that PIA can be obtained by polymerization in aqueous medium at pH = 2 initiated with potassium persulphate. The synthesized polymer was examined by NMR and FT-IR spectrometry. However, its experimental acid number (mg KOH/sample weight) determined by titration amounted only to about a half of the calculated theoretical value even after correction for the amount of water. According to the authors the phenomenon is related to intermolecular interactions but not with decarboxylation, and two carboxylic groups are present in one unit of PIA.

Mao Ziping and Yang [5] have reported that PIA could be obtained by polymerization of IA in water initiated with the redox system: K₂S₂O₈ and NaH₂PO₂. The authors did not isolate PIA but applied its solution for the impregnation of cotton fabric.

In this work we have decided to prepare PIA by different methods and conditions of synthesis and to check the structure of the resultant products by ¹H NMR, ¹³C NMR and FT-IR spectroscopy, elemental analysis, titration and size exclusion chromatography.

EXPERIMENTAL

Materials

Itaconic Acid (Koch-Light Lab. Ltd England); persulphate ammonium (analytical grade FOCh Poland); sodium hypophosphite (Riedel-de Haen, Germany); acetyl chloride (lab. grade FOCh), xylene (lab. grade, FOCh), were used without further purification.

Dioxan was distilled before used.

2,2'-Azobisisobutyronitrile (AIBN) was crystallized from absolute ethanol (lab. grade, FOCh).

Synthesis of poly(itaconic acid)

Polymerization in aqueous solution — method A

The polymerization was carried out by a similar method to that one described by Marvel and Shepherd [1]. Namely 10 g (77 mmoles) of itaconic acid was placed into a flask, and 50 cm³ of 0.5 M HCl and 2.2 mmoles of persulphate of ammonium were added. The content was heated at temperature of 60 °C for 30 hours. The product (PIA A) was precipitated with acetone, and dried over-

night at 50 °C under pressure *ca.* 1 hPa. The efficiency was 16 %.

Polymerization in dioxan — method B

10 g KI in 20 cm³ dioxan was heated for 22 hours at 60 °C. The quantity of the initiator (AIBN) was 0.8 % in relation to the monomer. The product (PIA B) obtained was separated from the monomer by precipitation, washed with acetone and dried overnight at 50 °C under pressure *ca.* 1 hPa. The efficiency was about 32 %.

Preparation by the hydrolysis of poly(itaconic anhydride) — method C

The synthesis was carried out similarly to that described in [5], in three steps: synthesis of itaconic anhydride, polymerization of itaconic anhydride, hydrolysis of poly(itaconic anhydride) (PIAn) to PIA.

Step one — 26 g of IA, 20 mL of acetyl chloride and 120 mL of xylene were refluxing at 70 °C for 20 h. After that time the solution was cooled and crystalline product was recrystallized from warm xylene. Next 7.5 g of itaconic anhydride from first step, 83 mL of xylene and 0.17 g of AIBN were heated at 60 °C for 16 h. PIAn was filtered, washed with xylene and ethyl ether, and dried under reduced pressure. The final product PIA C was obtained by mixing of poly(itaconic anhydride) with excess of water. The clear solution was kept overnight and excess water was evaporated at ambient temperature under reduced pressure and then dried overnight at 50 °C under pressure *ca.* 1 hPa.

Preparation by initiation with redox system — method D

The first part of the synthesis was carried out as in [5], namely 12.5 g of IA, 32.5 mL of water and 5 g of NaH₂PO₂ were heated at 65 °C. Then 1.6 g of K₂S₂O₈ in 10 mL of water was added and the solution was heated for 60 min. The polymer (PIA D) obtained was precipitated and washed with acetone and dried overnight at 50 °C under pressure *ca.* 1 hPa.

Methods

NMR

NMR spectra were performed using Bruker 250 MHz spectrometer in D₂O solutions.

Accepting the assumptions published in [4] (178.6 ppm — *rr* triad; 178.2 ppm — *mr* triad and 177.6 ppm — *mm* triad) the lengths of corresponding sequences were calculated using the equations:

$$\bar{n}_m = (mm + 0,5 mr) / 0,5 mr \quad (1)$$

$$\bar{n}_r = (rr + 0,5 mr) / 0,5 mr \quad (2)$$

$$\bar{n} = 1 / (rr + 0,5 mr) \quad (3)$$

Titration

Potentiometric and conductometric titrations with 0.1 M NaOH in aqueous solution were performed using CX-551 Elmetron microcomputer system.

The results of potentiometric titration of the samples under investigation are plotted in Henderson—Hasselbach's coordinates.

A simple Henderson's equation has been frequently used to characterize potentiometric titration data of polyelectrolytes [6].

Experimental data of potentiometric titration were calculation applying the simple Henderson equation to calculate the apparent ionization constant pK_{app} :

$$pH - \log \frac{\alpha_N}{1 - \alpha_N} = pK_{app} \quad (4)$$

where: α_N — fraction of ionizable sites on poly(itaconic acid) which are not neutralized by H^+ .

The results of conductometric titration were calculated as a per cent of carboxylic groups referred to two groups in one unit [Formula (II)].

FT-IR

FT-IR spectra were performed using Perkin-Elmer System 2000. The samples investigated were formed as KBr pellets. Comparatively, two D samples, dried at different conditions [one of them typically (overnight, 50 °C/1 hPa), the other at elevated temperature (5 h, 120 °C/atmosphere pressure)] were investigated.

SEC

Size exclusion chromatography was carried out using Waters modular gel permeation chromatography system consisted of 510 pump, U6K injector, and 410 refractive-index detector. Two TosoHaas HXL G 4000 columns were used.

Relative molecular weights were determined by SEC after treating the samples with diazomethane in tetrahydrofuran (THF). The samples were dispersed in THF and a freshly prepared THF solution of diazomethane was added. The reaction mixture was left at room temperature until next day to ensure the reactions were completed. Sample D after treatment with diazomethane was partially insoluble and was not analyzed.

RESULTS AND DISCUSSION

IR spectra are presented in Fig. 1. As we can see from this Figure samples A—C show the same chemical structure.

Drying of PIA at higher temperature leads not only to anhydride formation, but also to decarboxylation as it is illustrated in Fig. 2. As we can see the bands related to anhydride structure 1860 and 1780 cm^{-1} (absent in Fig. 1) and decarboxylation at 2342 cm^{-1} (CO_2 occluded in KBr pellet) appear in spectrum of curve 2.

The results of elemental analysis are listed in Table 1. As we can see, the results of sample D differ substantially from the others. An additional analysis shows that a substantial amount of phosphorous and metal residua are present, and it is difficult to purify this sample of

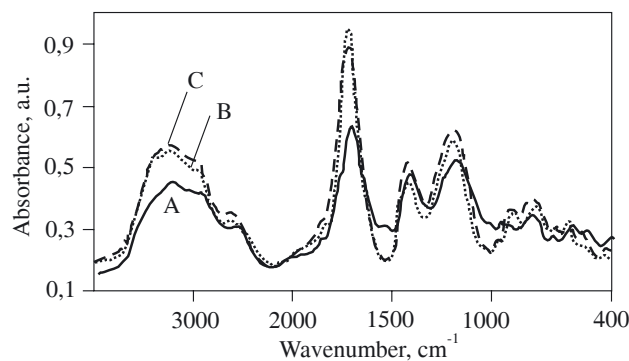


Fig. 1. FT-IR spectra of samples A, B and C

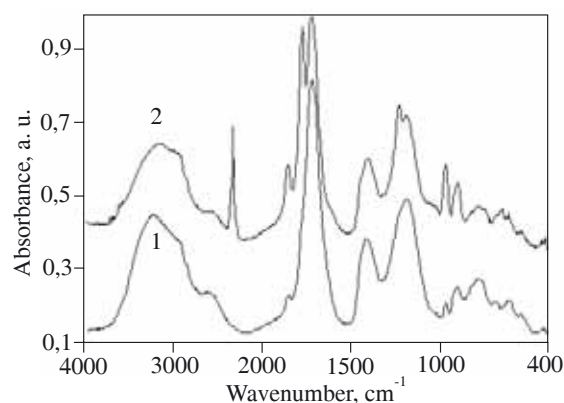


Fig. 2. FT-IR spectra of sample C: 1 — dried overnight at 50 °C under 1 hPa, 2 — dried 5 h at 120 °C under atmospheric pressure

PIA. For this reason the sample D was not investigated in detail.

Table 1. Elemental analysis, molecular weights and conductometric titration results of PIA

Sample	C, %	H, %	\overline{M}_w	\overline{M}_n	% of $-COOH^*)$
A	43.9	5.24	25 210	16 290	69.1
B	43.6	4.95	7 270	5 138	74.1
C	46.1	4.92	16 850	12 810	67.4
D	24.6	3.46	—	—	39.5

*) Relative per cent part converted into the content of $-COOH$ groups in the structure described by Formula (III)

In contrast, sample C shows a very good agreement with that calculated for structure (III) (theoretical C 46.15 %; H 4.62 %). The difference between these results and those published in [3] (C 39.89—41.19 %; H 5.11—5.30 %) is perhaps related to the method of drying, and corresponds to the product with units hydrated by one molecule of water as it was suggested by the authors of [3]. Samples A and B show a lower per cent of carbon, which cannot be explained by partial decarboxylation, because all structures presented as structure (II) predict

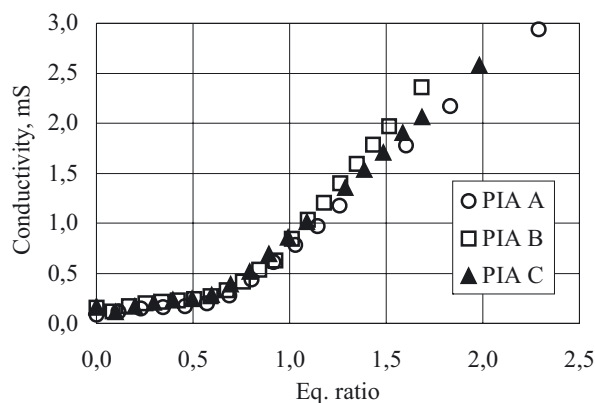


Fig. 3. Conductometric titration of samples A, B and C

higher per cent of carbon (from 50 % for unit d to 57.1 % for unit b). The results obtained correspond to the structure in which one molecule of water is connected with two units of PIA (calculation: C 43.16 %; H 5.04 %).

The phenomenon that only about 2/3 of the predicted groups can be found by titration has been explained by Braun and Sayed [2] assuming the structures presented in Formula (II).

We can see also that there are not very different amounts of carboxylic groups accessible for titration in samples A—C obtained by various methods. As well the differences in molecular weights of the samples, determined by SEC method (Table 1), do not influence those amounts.

The result of conductometric titration presented in Fig. 3 confirms the above conclusion, that approximately 2/3 of carboxylic groups can be neutralized. It is in accordance with the assumption that ionization of a carboxylic group situated between two ionized groups is retarded and is in agreement with the statistics of substitution of polymers [9].

In the latest publications [4, 5] it has been suggested that partial neutralization of PIA reduced the dissociation constants of the free carboxylic groups in the molecule. The greater the number of carboxylic groups neutralized, the less acidic is PIA.

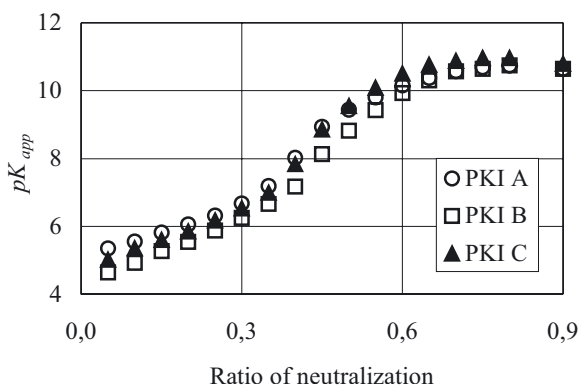


Fig. 4. Results of potentiometric titration using Henderson—Hasselbach plot

Experimental data of potentiometric titration were calculated and presented in Fig. 4. It is known that the deviation from the linearity for poly(methacrylic acid) [7] and poly(α -L-glutamic acid) [8] has been interpreted in terms of conformational changes in the macromolecules.

Figure 4 shows that only small differences between the samples under investigation exist. In all cases one can observe a deviation from the linear plot corresponding to equivalent ratio equal to only 0.66 (not 1.0). It could possibly show that conformational change occurs.

^1H NMR spectra of all samples show two broad peaks approximately of the same intensity, within the range from 2.4 to 2.7 ppm, which can be referred to methylene groups in the main chain and in pendant groups or groups in the cyclic structure.

^{13}C NMR spectra (Fig. 5) show also two peaks of two methylene groups (40—50 ppm) and two multiplet peaks in the range from 173 to 178 ppm, which can be referred to the two types of carbonyl groups present in

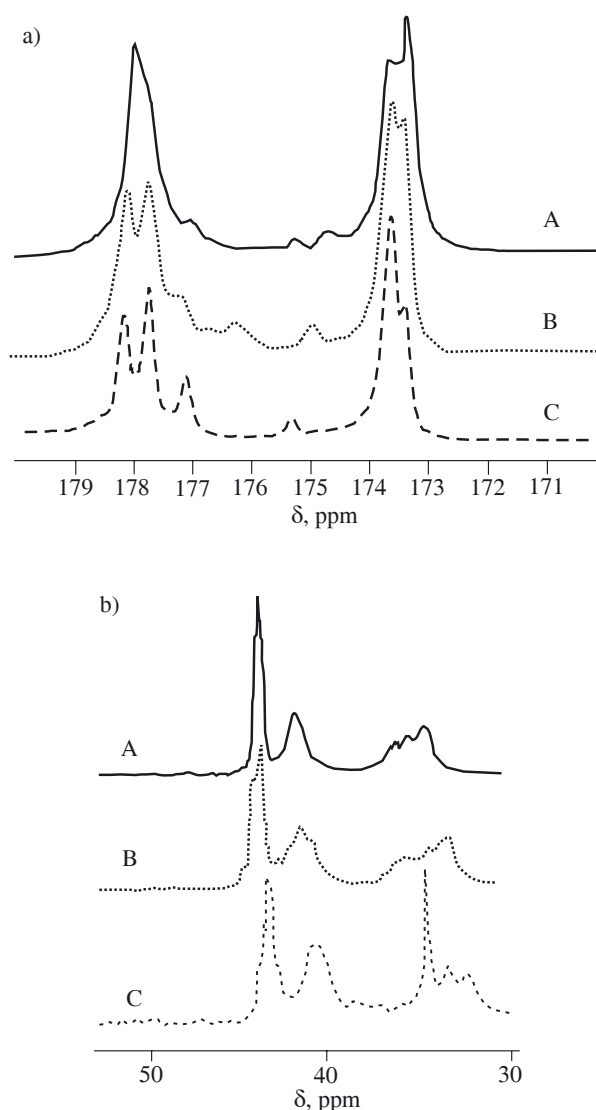


Fig. 5. ^{13}C NMR spectra of PIA samples A—C; a) range of carbonyl groups, b) range of methylene groups

different triads. We can see that two types of carbonyl groups are present in samples under investigation almost in the same proportions. Differences in the range 40–50 ppm can be related to small differences in the structures of units produced by chain transfer process.

Table 2. Intensities of the corresponding bands of carboxylic carbons (a) of different PIA and corresponding lengths of sequences [4]

Sample	Assignment			Length of sequences		
	<i>rr</i> (a)	<i>mr</i> (a)	<i>mm</i> (a)	n_m	n_r	n
A	0.502	0.387	0.111	1.57	3.59	1.44
B	0.394	0.451	0.155	1.69	2.75	1.61
C	0.145	0.417	0.148	3.40	1.72	2.83

From the results presented in Table 2 it follows that PIA obtained from polyanhydride (sample C) contains less *rr* sequences than samples A and B. However, differences in the structures of the samples under investigation can relate not only with sequences distribution, but also with differences in the structures of units generated by chain transfer during polymerization. For this reason deeper analysis of sequences distribution seems to be connected with rather high error.

CONCLUSIONS

The synthesis of poly(itaconic acid) in polymerization initiated by a big amount of strong redox system leads to a product with complicated structure (sample D) that is different from that of the sample B obtained with the use of AIBN as an initiator. PIA obtained in water (A) and in dioxane (B) as well as those prepared by the hydrolysis of poly(itaconic anhydride) (C) contain two carboxylic groups per polymer unit, but only about 2/3 of carboxylic groups are accessible for conductometric and potentiometric titrations.

It is known that PIA is very hygroscopic. It has been found [1, 3] that different amounts of water are combined with a single unit of PIA. It seems then that de-

pending on the method of drying the amount of water could be different, and it leads to the different results of titration published in the literature. It seems to be of importance to use a standard method of drying.

Based on the results of elemental analysis of PIA samples obtained by various methods it has been found that it was not possible to explain the phenomenon of the reduction of accessible carboxylic groups by decarboxylation and cyclization proposed by Braun and Sayed [2].

The results obtained by titration, ^1H NMR, ^{13}C NMR analysis confirm that samples A–C are atactic and contain two types of neighbourhood of methylene and carboxylic groups.

The fact that only 2/3 of carboxylic groups is accessible for neutralization seems to be related to the conformational changes in the macromolecule of PIA.

A deeper analysis including the examination of properties of PIA in solution seems to be important and will be a subject of our future investigations.

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