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## Study of poly(itaconic acid) in aqueous solutions

**Summary** — Poly(itaconic acid) (PIA) have been synthesized by hydrolysis of poly(itaconic anhydride) and by polymerization of itaconic acid initiated by redox system. Conductometric, potentiometric and spectrophotometric titration of aqueous solutions of PIA have been carried out. The results are discussed in terms of a conformational transition. Apparent dissociation constant and conductance of PIA solutions have been investigated as functions of concentration.

**Key words:** poly(itaconic acid), aqueous solutions, dissociation constant, equivalent conductance, conformational transition.

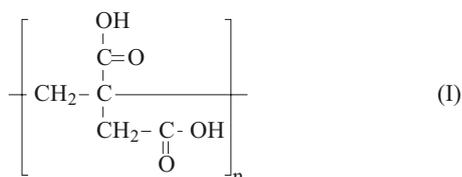
### BADANIA POLI(KWASU ITAKONOWEGO) W ROZTWORACH WODNYCH

**Streszczenie** — Przeprowadzono syntezy poli(kwasu itakonowego) poprzez hydrolizę poli(bezwodnika kwasu itakonowego) oraz na drodze polimeryzacji inicjowanej układem redoks. Wykonano miareczkowania konduktometryczne, potencjometryczne i spektrofotometryczne roztworów wodnych otrzymanych polikwasów. Stwierdzono, że badane polikwasy zawierają około 66 % dostępnych grup karboksylowych (rys. 1 i 7). Wysunięto hipotezę o przemianie konformacyjnej, która powoduje niedostępność pozostałych grup karboksylowych. Wyznaczono zmiany potencjału termodynamicznego związanego z taką przemianą  $\Delta G = 5,4\text{--}5,9$  kJ/eq (tabela 1, rys. 4 i 5). Badano przewodnictwo elektryczne roztworów polikwasów (rys. 8 i 9) i zaobserwowano liniową zależność odwrotności przewodnictwa równoważnikowego od pierwiastka kwadratowego ze stężenia PIA.

**Słowa kluczowe:** poli(kwas itakonowy), roztwory wodne, stała dysocjacji, przewodnictwo równoważnikowe, przemiana konformacyjna.

In the early studies on the polymerization of itaconic acid [1–3], it has been suggested that during polymerization cyclic structures were formed [2], decarboxylation took place [3], the resultant polymer was strongly hydrated and anhydride structures were formed during water removal.

However, further studies have proven that poly(itaconic acid) (PIA) could be obtained by polymerization of itaconic acid (IA) in water, initiated with potassium persulphate, by polymerization in organic solvents, initiated with 2,2'-azobisisobutyronitrile (AIBN), as well as by hydrolysis of poly(itaconic anhydride) prepared by polymerization of itaconic anhydride. It has been shown that the polymers obtained by various methods were really PIA of the following structure:



and in particular, when appropriate conditions were used, neither significant decarboxylation took place dur-

ing polymerization as previously suspected [2, 3] nor any formation of anhydride structures could be observed. On the other hand, based on  $^{13}\text{C}$  NMR [4–6], one can find that PIA polymers show different tacticity depending on the synthesis process.

According to paper [2] decarboxylation results from thermal degradation taking place at elevated temperature, but when the polymerization is carried out at a low temperature or by hydrolysis of poly(itaconic anhydride) and the product is dried at temp. below 60 °C under pressure of 1 hPa one can obtain PIA showing the structure as given above. An additional, very convincing argument for this structure is the founding [8] that methyl diester can be obtained by treating the product of itaconic acid polymerization with diazomethane. On the other hand, it has been found [2, 3, 5, 6] that both conductometric and potentiometric titrations of PIA provide a result suggesting that the product contains only 50–60 % of carboxylic groups resulting from the unit structure.

Based on literature reports and our own studies, one can assume that PIA which structure would be most consistent with that shown above can be prepared by hydrolysis of poly(itaconic anhydride) [8] followed by dry-

ing under appropriately selected conditions of temperature and pressure. Such a method was used in this work. In this situation it was of interest to examine the behavior of PIA in aqueous solutions. Literature reports on this topic are rather very rare [7], while numerous reports on polyacid solutions concentrate mainly on the properties of solutions of polymers such as poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA), poly(L-glutamic acid) or polylysine. The latter polymers have been studied in terms of possible occurrence of a helix structure [8–10]. From the literature [8–12] it follows that in the case of PMA a conformational conversion is observed when the ionization degree is changed.

As it is known, for aqueous solutions of organic acids one can define apparent dissociation constant ( $K_{app}$ ) which in the case of polyacids has a character of apparent constant being dependent of concentration ( $c$ ). If  $\alpha$  is the dissociation degree, for very weak acids  $c(1 - \alpha) \approx c$  and hence pH may be given in the following form:

$$\text{pH} = 1/2 (\text{p}K_{app} - \log c) \quad (1)$$

Conformational conversions taking place with the change in the ionization degree ( $a$  defined as a fraction of ionized acid groups) observed during potentiometric titration have been found mostly on the basis of the deviation from the classical equation of Henderson-Hasselbach that is a transformation of equation (1) into the form:

$$\text{p}K_{app} = \text{pH} - \log \frac{a}{1-a} \quad (2)$$

supplemented with a unit that includes the additional free energy ( $\Delta G$ ) connected with interactions at the given degree of ionization:

$$\text{p}K_{app} = \text{pH} - \log \frac{a}{1-a} - \frac{0.43}{RT} \Delta G \quad (3)$$

where:  $R$  — universal gas constant,  $T$  — temperature in K.

For PMA these deviations occurred at low ionization degrees ( $a < 0.4$ ). In UV spectrometric measurements with various ionization degrees [13], a non-linear relationship of absorbance has been observed within the range of wavelength ascribed to the absorption of  $-\text{COO}^-$  and  $-\text{COOH}$  groups.

In the present work we decided to use these methods to examine aqueous solutions of PIA, including also measurements of the conductivity of these solutions.

As it is known, simple Debye-Hückel's equation is not satisfied for polyelectrolytes

$$\Lambda = \Lambda_0 - k\sqrt{c} \quad (4)$$

where:  $\Lambda$ ,  $\Lambda_0$  — molar conductivity and limiting molar conductivity,  $c$  — concentration of electrolyte.

According to the theory suggested in the literature [15, 16], a better approximation (linearization) can be obtained when the inverse of  $\Lambda$  is plotted as a function of square root of concentration.

## EXPERIMENTAL

### Materials

Itaconic acid (Koch-Light Lab., England) and xylene, lab. grade (POCh) were used without further purification.

Acetone was dried under anhydrous  $\text{MgSO}_4$  and distilled before use.

AIBN (Merck-Schuchardt, Germany) was crystallized from absolute ethanol.

Itaconic anhydride was prepared by refluxing a mixture of itaconic acid and acetyl chloride as described in [8] and then it was recrystallized twice from warm xylene.

Poly(acrylic acid) ( $M_w = 44\,800$  Da) was obtained by polymerization of acrylic acid in toluene initiated by AIBN.

### Synthesis of poly(itaconic acid)

The synthesis of poly(itaconic anhydride) was carried out similarly to that described in [8]. 7.5 g of itaconic anhydride, 83 mL of xylene and 0.17 g of AIBN were heated at 60 °C for 16 h. The polymer precipitated was filtered, washed with xylene and ethyl ether and then dried under reduced pressure.

Three kind of PIA numbered from 1 to 3 were prepared.

First one was obtained by mixing poly(itaconic anhydride) with excess of water. The clear solution was kept overnight and excess of water was evaporated at ambient temperature under reduced pressure (PIA 1).

A portion of the obtained PIA 1 was fractionated by precipitation from aqueous solution with anhydrous acetone. Eight fractions were obtained, of which only the middle fraction (Fraction 5) was used for further examinations (PIA 2).

Sample PIA 3 was synthesized as in paper [4]. The polymerization was carried out in 0.1 M aqueous HCl solution, using  $\text{K}_2\text{S}_2\text{O}_8/\text{K}_2\text{S}_2\text{O}_5$  as initiator. The process was carried out for 48 h at room temperature. The solution was concentrated at a low temperature under vacuum, the polymer was precipitated with acetone and then it was redissolved in water followed by precipitation with acetone.

All the samples were dried at temperature of 50 °C under reduced pressure (about 1 hPa). It has been previously found [5] that under such conditions crystallization water was removed without decarbonization.

### Methods

NMR spectra were performed in  $\text{D}_2\text{O}$  solutions, using Bruker 250 MHz spectrometer.

Potentiometric and conductometric titrations were performed using CX-551 Elmetron microcomputer sys-

tem. All titrations were made using 0.1 M NaOH or 0.1 M  $(\text{CH}_3)_4\text{NOH}$ .

FT-IR spectra were taken using Perkin-Elmer System 2000.

Size exclusion chromatography (SEC) was carried out with Waters's modular gel permeation chromatography system, consisted of a 510 pump, a U6K injector and a 410 refractive index detector. Two TosoHaas HXL G 4000 columns were used.

## RESULTS AND DISCUSSION

### Characteristics of PIA samples

Based on  $^1\text{H}$  NMR spectra, it was found that the monomer content in all the samples used in the further part of the study did not exceed 0.5 %. The peak of protons of  $\text{H}_2\text{C}=\text{C}<$  group within bands 6.38 and 5.90 ppm was analysed.

Elementary analysis and determination of molecular weight were performed for all the samples and the results are given in Table 1.

Table 1. Characteristics of PIA samples

Sample	% C	% H	$M_w$	% $\text{COOH}^*$
PIA 1	46.1	4.92	16 850	66.3
PIA 2	44.1	5.51	12 080	67.7
PIA 3	44.7	5.47	20 480	66.2

<sup>a</sup>) Determined at a concentration of 0.0125 eq/L.

To find the percentage content of accessible carboxylic groups conductometric titration was also carried out. The titration was performed for various concentrations of PIA in water ranging from 0.0125 to 0.001 eq/L. All the results showed a content of accessible carboxylic groups at a level 66 % within the error limits  $\pm 2$  %. As an example the results for PIA 1 and PIA 3 samples are shown in Fig. 1.

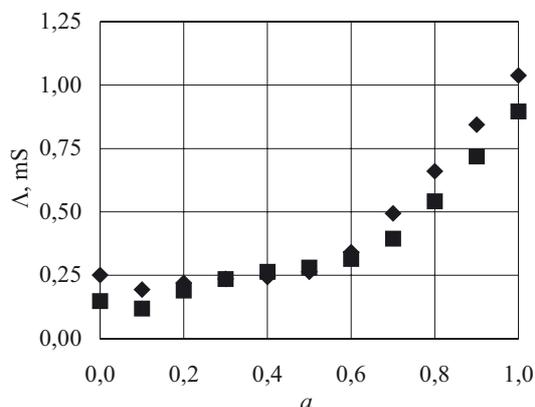


Fig. 1. Conductometric titration of 0.0125 eq/L aqueous solutions of PIA with 0.1 M NaOH;  $\blacklozenge$  — PIA 1,  $\blacksquare$  — PIA 3

### Determination of the dissociation constant of PIA

Determinations of pH for PIA 2 solutions were performed depending on concentration and the values of  $\text{p}K_{\text{app}}$  were calculated according to eq. (1). The results are shown in Fig. 2.

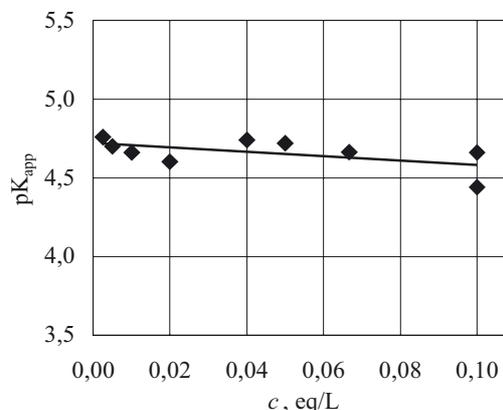


Fig. 2. Dependence of  $\text{p}K_{\text{app}}$  on PIA 2 concentration

The value of  $\text{p}K_{\text{app}}$  slightly decreases with concentration. For  $c = 0$   $\text{p}K_{\text{app}} = \text{p}K^0$  is 4.52. Similar determinations were carried out for itaconic acid (monomer). The obtained value of  $\text{p}K^0$  was 3.89 being consistent with that reported in the literature [14] the first dissociation constant  $\text{p}K_1 = 3.85$ .

The results of pH measurements for a wider range of concentration of PIA 3 are shown in Fig. 3.

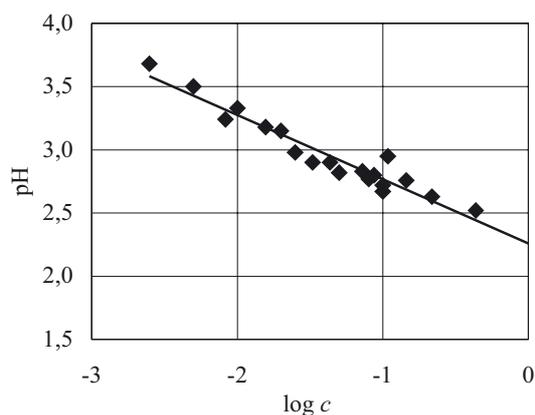


Fig. 3. Dependence of pH on PIA 3 concentration

According to eq. (1) we can find by extrapolation to  $\log c = 0$  (thus  $c = 1$  eq/L) that  $\text{p}K_{\text{app}}$  for PIA 3 is 4.47.

### Potentiometric titration of PIA

The obtained results of potentiometric titration of PIA with NaOH were calculated according to eq. (2). The results obtained for various concentrations of PIA 2 are

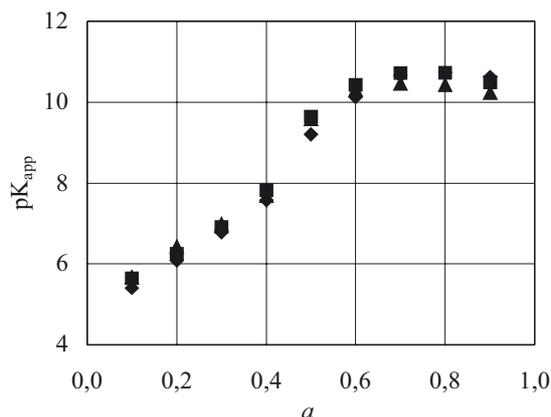


Fig. 4. Henderson-Hasselbach's diagram for PIA 2;  $\blacklozenge$  — 0.0125 eq/L,  $\blacksquare$  — 0.005 eq/L,  $\blacktriangle$  — 0.025 eq/L

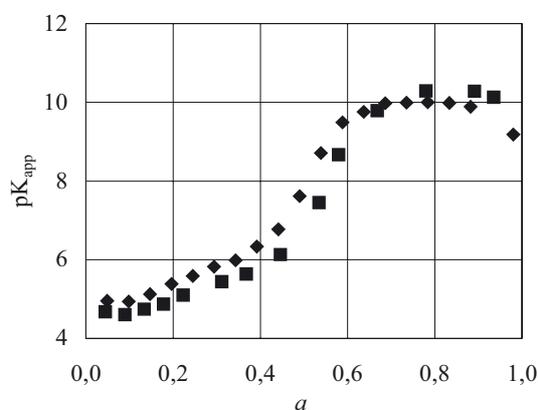


Fig. 5. Henderson-Hasselbach's diagram for titration of PIA 3 with  $\blacklozenge$  —  $(\text{CH}_3)_4\text{NOH}$ ;  $\blacksquare$  — NaOH; concentration of PIA 3  $0.74 \cdot 10^{-3}$  eq/L

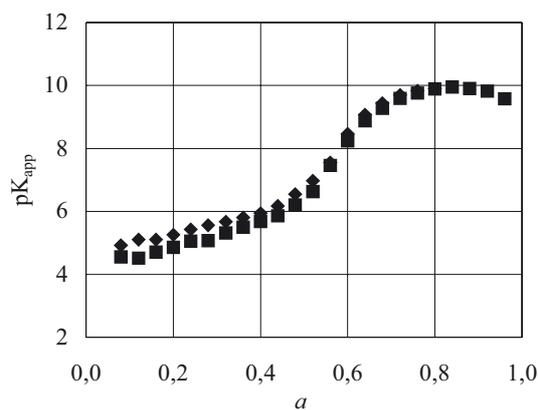


Fig. 6. Examination of hysteresis by:  $\blacklozenge$  — titration with NaOH;  $\blacksquare$  — back titration by HCl

shown, as an example, in the Fig. 4 versus ionization degree.

Similarly, potentiometric titration of PIA 3 with  $(\text{CH}_3)_4\text{NOH}$  was performed and compared in Fig. 5 with PIA 3 titrated with NaOH.

In addition titration with NaOH was carried out as previously followed by back titration of the solution

with HCl. As it is shown in Fig. 6 no hysteresis was found and a slight shift seemed to be due to the presence of some low quantity of electrolyte (NaCl) resulted from neutralization.

Table 2. Free energy of the conformation conversion of PIA

Sample	Base titrant	$\Delta G$ , kJ/eq	$c$ , eq/L
PIA 1	NaOH	5.86	0.0125
PIA 1	$(\text{CH}_3)_4\text{NOH}$	5.92	0.0074
PIA 2	NaOH	5.82	0.005
PIA 2	NaOH	5.36	0.0125
PIA 3	NaOH	5.62	0.001
PIA 3	NaOH	5.70	0.0125

The results obtained were used to calculate  $\Delta G$  according to eq. (3) as it was described in [11–13] from the area between the straight line extrapolated from the first portion of the diagram and the curve obtained. The results of  $\Delta G$  calculations are listed in Table 2.

### Spectrophotometric titration of PIA

The spectrophotometric titration of PIA was carried out using UV by method described in paper [13]. To verify this method, the spectrophotometric titration of poly(acrylic acid) (PAA) which is free from the conformational conversion was performed. In accordance to [13] it was found that the absorbance related to COOH groups decreased, while the absorbance within 195 and 200 nm ascribed to  $\text{COO}^-$  ions increased linearly. The result for PIA is different as compared with PAA. Reduced absorbance  $A' = A/bc$  was calculated and plotted against degree ionization —  $a$  (where  $b$  is optical path length in the titration cell and  $c$  is concentration of PIA in eq/L). An example of sample PIA 2 is shown in Fig. 7.

As it is seen, in the case of PIA 2 the absorbance is practically constant at 220 nm ( $\text{COOH}$  groups), but a strong increase in absorbance is observed at 195 and

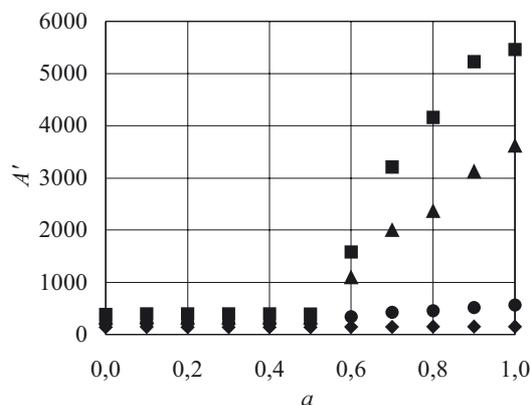


Fig. 7. Reduce absorbance ( $A'$ ) versus ionization degree ( $a$ ):  $\blacklozenge$  — 220 nm;  $\bullet$  — 210 nm,  $\blacktriangle$  — 200 nm,  $\blacksquare$  — 195 nm

200 nm when the ionization degree exceeds 0.6, *i.e.* within the range where an abnormal increase in pH during potentiometric titration takes place. This phenomenon was observed for all PIA samples under investigation. It is difficult to assume that such a considerable increase in  $\text{COO}^-$  ions could take place in this region. Such an abnormal increase in absorbance within this range seems to be associated with the formation of cyclic structures with a high coefficient of specific absorbance. However, such a hypothesis would require a confirmation by another method. Similar results were obtained for all the samples.

### Examination of the conductivity of PIA solutions

In order to supplement the results given above, the conductivity of PIA aqueous solutions was measured. The electrolytic conductivity of PIA aqueous solutions was determined and the equivalent conductivity was calculated. The calibration of conductometer was performed using aqueous solutions of KCl. The dependence of equivalent conductivity is shown in Fig. 8.

As it is seen, Debye-Hückel's relationship (eq. 4) is not satisfied and the limiting conductivity cannot be determined.

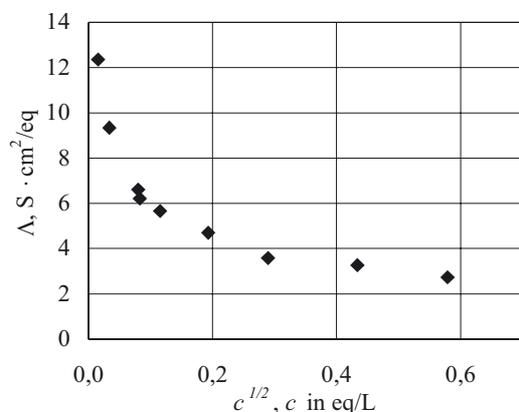


Fig. 8. Equivalent conductivity ( $\Lambda$ ) of PIA 2 solutions versus square root of concentration ( $c^{1/2}$ )

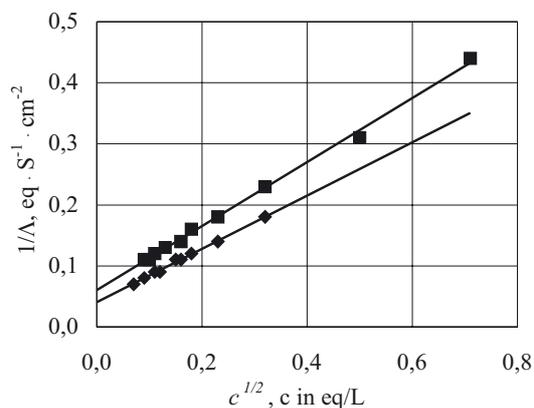


Fig. 9. Dependence of  $1/\Lambda$  on  $c^{1/2}$  for:  $\blacklozenge$  — PIA 2;  $\blacksquare$  — PAA

In accordance with the theory suggested in the literature [15, 16], a better approximation (linearization) can be obtained in the system with the inverse of  $\Lambda$  as a function of square root of concentration:  $\Lambda^{-1} = f(c^{1/2})$ .

Figure 9 shows the correlation between  $1/\Lambda$  and the square root of concentration for PIA 2 and compared with similar function for PAA.

The free term was used to calculate the limiting equivalent conductivity  $\Lambda_0$  of PIA, equal to  $29.5 \text{ S} \cdot \text{cm}^2 \cdot \text{eq/L}$  and seems to be slightly higher than for PAA ( $18.4 \text{ S} \cdot \text{cm}^2 \cdot \text{eq/L}$ ).

These results are useful only to estimate the value of  $\Lambda_0$ , and the determination of more precise value requires further examinations.

### CONCLUSIONS

It has been found that PIA obtained by the hydrolysis of poly(itaconic anhydride) and that prepared by polymerization in water initiated with the redox system do not differ significantly in their properties. All the examined samples showed a content of accessible carboxyl groups at a level of 66 % during conductometric titration. The determined  $\text{p}K^0$  is 4.52, while at the concentration  $C = 1 \text{ eq/L}$ ,  $\text{p}K_{\text{app}} = 4.47$ . In the case of potentiometric titration, one can observe deviation from the classic Henderson-Hasselbach equation for all the samples investigated. No hysteresis was observed. Assuming that this deviation results from the conformational conversion, the change in the conformational energy has been calculated to be  $\Delta G = 5.4\text{--}5.9 \text{ kJ/eq}$ , but no significant changes in this values was observed with changing concentration or replacing  $\text{Na}^+$  with  $(\text{CH}_3)_4\text{N}^+$ . From the measurements of conductivity of aqueous PIA 2 solutions  $\Lambda_0$  of PIA 2 was estimated as equal to  $29.5 \text{ S} \cdot \text{cm}^2 \cdot \text{eq/L}$  and seems to be higher than that value for PAA ( $18.4 \text{ S} \cdot \text{cm}^2 \cdot \text{eq/L}$ ).

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### W kolejnym zeszycie ukaza się m.in. następujące artykuły:

- Termoplastyfikacja skrobi na drodze wytlaczania w obecności plastyfikatorów
- Nowe optycznie czynne poli(estroimidy) i poli(amidoimidy) Cz. II. Synteza optycznie czynnych polimerów
- Otrzymywanie i charakterystyka kopoliestrów z poli(bursztynianu butylenowego) i poli(tereftalanu butylenowego) (*j.ang*)
- Wpływ pochodnej bis(2-oksazoliny) jako kompatybilizatora oraz warunków wytłaczania reaktywnego na właściwości mieszanin poliamid 6/poli(tereftalan etylenu)
- Badanie powierzchni politetrafluoroetyleny metodą rozpraszania promieniowania rentgenowskiego (*j. ang*)
- Reometryczne badania procesu żelowania kompozycji o wzajemnie przenikających się sieciach polimerowych otrzymanych z poliuretanu i nienasyconego poliestru
- Badanie procesu wytwarzania nanokompozytu polipropylenu z montmorylonitem