Vol. 1, No. 3, 2007 Chemistry

Michael Bratychak[1, 2], Witold Brostow[1, 2], Dorota Pietkiewicz[1] and Petro Topilnytskij[2]

POLYESTERS ON THE BASIS OF PETROLEUM RESIN AND POLYETHYLENE GLYCOLS

[1] Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas, Denton, TX 76203-5310, USA; brostow@unt.edu;
[2] Department of Petroleum Chemistry and Technology, Lviv Polytechnic National University, 12, St. Bandery, 79013 Lviv, Ukraine; mbratych@polynet.lviv.ua

Received: September 29, 2007

Abstract. New polyesters have been obtained on the basis of petroleum resin with carboxyl groups and polyethylene glycols. The average molecular mass of the petroleum resin is 1050, its functionality = 1.74. Optimal for the polyesters synthesis is the equimolar ratio between the initial compounds. The reaction is performed in the melt in the presence of *p*-toluenosulphuric acid as the catalyst. In the optimal temperature range 423-463 K the yield of the process ranges from 91 to 94 % depending on the conditions. The rate of the polyester formation reaction practically does not depend on the length of the acids or the glycol chain molecules. The functionality is the decisive factor. We report the degrees of polycondensation of the new polyesters.

Key words: polyester, resin, glycols, polycondensation, adypic acid, carboxyl group

1. Introduction

Polyesters are thermoplastic and thermosetting polymers containing a polar ester -CO-O- groups in the main polymer chain. The ester groups provide inter- and intramolecular chain interactions that are reflected in the mobility of chains and crystal forms. It is for this reason that these polymers can form strong fibers in addition to being extensively used in the form of sheets [1]. Semi-rigidity leading to the formation of polymer liquid crystals (PLCs) can be achieved, providing an extra dimension in property control – as discussed by Hess and his coworkers [2–4].

Polyesters can be obtained from two monomers, namely dicarboxylic acids (its methyl ester or chloride) and glycols in the presence of a catalyst by polycondensation. The presence of polyesters with their ester bonds leads to products with good physical and mechanical properties. Apart from fibers and sheets, polyesters are used among others for the production of films, molding materials, varnishes and protective coatings [5, 6]. The most important polyesters produced commercially are:

- poly(ethylene terephthalate) (PET) which has found a wide range applications because of its good balance of properties and the possibility of controlling the degree of crystallinity and the level of orientation. PET is used as fibers, film for electrical insulation, packaging, recording tape, bottles;
- poly(butylene terephthalate) (PBT): the longer hydrocarbon chain of the butylene glycol renders the polymer molecules more flexible and less polar than PET. Major markets are electrical and electronic engineering and automotive applications;
- poly(ethylene naphthalene) (PEN) is a polyester with rapidly increasing use. PEN has a higher glass transition temperature Tg than PET and finds applications as jelly jars, sterilizing and returnable bottles [5, 6];
- ethylene-vinyl acetate (EVA) and its copolymers which have a good potential use as food packaging materials [7].

With the aim of an expansion of range of polyesters which could be used as surface-active substances, we have studied the possibility of obtaining such products on the basis of petroleum resins and polyethylene glycols. In this connection, the present work constitutes a part of a broader program aimed at obtaining oligoesters from a variety of monomers [8-11].

The reaction between petroleum resin and polyethylene glycol proceeds as follows:

$$HOOC\text{-}R_1\text{-}COOH + HO\text{-}R_2\text{-}OH \rightarrow$$
$$\rightarrow HO\text{-}R_2\text{-}O\text{-}CO\text{-}R_1\text{-}COOH + H_2O \quad (1)$$

As the catalyst we have used p-toluenosulphuric acid (*p*-TSA).

2. Experimental

2.1. Starting materials

We have used a PRCG (petroleum resin with carboxyl groups) that is a modified petroleum resin obtained by initiative cooligomerization of unsaturated compounds from hydrocarbon pyrolysis C_9 fraction. The

product contains reactive carboxyl groups – what gives the possibility of its application as a feedstock for polyesters production by polycondensation. The synthesis has been performed at Lviv Polytechnic National University.

PRCG is characterized by lower functionality in comparison with dicarboxylic acids (their functionality is equal 2). Therefore, we have investigated a parallel reaction between adypic acid and polyethylene glycol.

Products called PET-400 and PET-600 with the molecular masses 400 and 600, respectively, produced by Barva, Lviv, Ukraine, were studied. Their characteristics are summarized in Table 1.

Table 1

Characteristics of initial components for polyester synthesis

2.2. Experimental procedure

Polycondensation was performed in a four-neck reactor equipped with a mechanical stirrer, a thermometer, an inert gas bubbler and a reflux cooler with metering nozzle for control of the water amount. The reaction was carried out in a melt in the presence of catalyst (*p*-toluenosulphuric acid) which was loaded in the amount of 1.2 mol % with respect to the main component.

The reaction mixture was heated using a silicone oil bath. Calculated quantities of the acid and glycol were loaded into the reactor, a contact thermometer and reflux cooler were added, heating and stirring were switched on. The polycondensation reaction was carried out in the medium of nitrogen purified from oxygen and humidity by passing it through sulphuric acid and calcium chloride. The nitrogen was fed by a tube situated under the level of the reaction mass. An appropriate gas velocity was established to ensure the necessary stirring in the reactor and carrying away of steam so produced.

The polycondensation was carried out at 423 K during 1 hour. The acid numbers were determined periodically. For this purpose samples of the reaction mixture were taken every 15 minutes, then loaded to previously weighted flasks and their masses determined. Each sample was dissolved in acetone or dioxane and titrated by 0.1 N solution of potassium hydroxide in the presence of phenolphthalein. Acid numbers were calculated as:

$$AN = M_{KOH} \cdot F / M \cdot 10^{-3} \qquad (2)$$

where AN is the acid number in mg KOH/g; M_{KOH} is the molecular mass of potassium hydroxide (M_{KOH} = 56.11); M is the molecular mass of AA or PRCG and F is the functionality.

Curves showing dependence of the acid number on the time were plotted on the basis of the data so obtained. The degree of polycondensation for every experimental point was calculated and dependence of the degree of polycondensation on the time was plotted. Rate constants were calculated as:

$$k = (tg\alpha / C_o) / Ck \qquad (3)$$

where k is the rate constant in kg^2/(mol^2·s); α is the slope of the curve of the dependence of the degree of polycondensation on the time; C_o is the initial concentration of carboxy-containing compound, in mol/kg; C_k is the catalyst concentration, in mol/kg.

3. Results and Discussion

Figure 1 shows the change of polycondensation degree of polyesters synthesized on the basis of adypic acid (AA) and polyethylene glycol (PEG-600). We see the excess of either initial agent produces polyesters with lower molecular mass. The reason is the decrease of polycondensation degree. Therefore, it is necessary to carry out the polycondensation process with the equimolar ratio of the components to obtain oligomers with highest molecular masses.

Figure 2 shows the dependence of acid number upon the time for the reaction between PEG-400, PEG-600 and PRCG with adypic acid.

The data obtained were used to create a diagram of polycondensation degree as a function of time (see Fig. 3) and to calculate the effective rate constants (see Table 2).

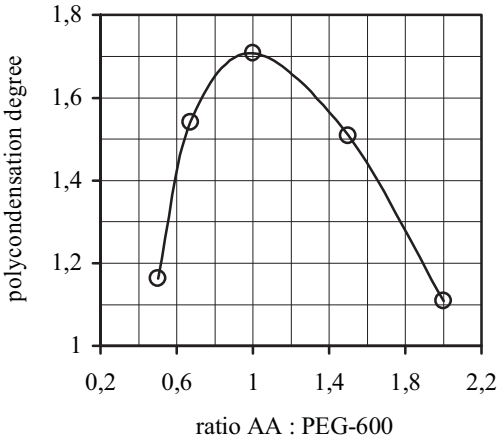

Fig. 1. Dependence of the polycondensation degree on the ratio AA : PEG-600 at 423 K

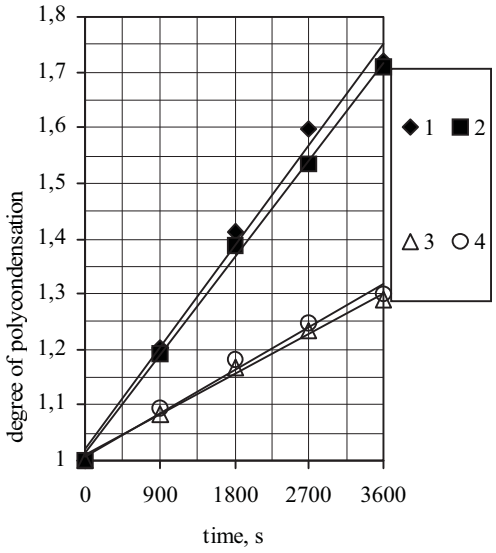

Fig. 3. Dependence of the polycondensation degree on the reaction time at 423 K for the polycondensation reactions: AA + PEG-400 (1); AA + PEG-600 (2); PRCG + PEG-400 (3); PRCG + PEG-600 (4)

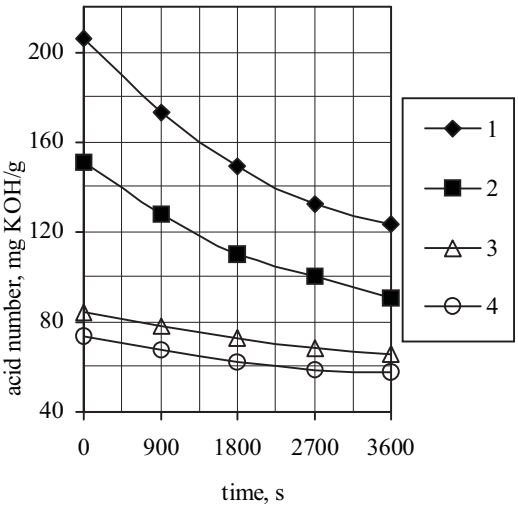

Fig. 2. Dependence of the acid number on reaction time at 423 K for the polycondensation reactions: AA + PEG-400 (1); AA + PEG-600 (2); PRCG + PEG-400 (3); PRCG + PEG-600 (4)

Table 2

Effect of the component nature on the degree of polycondensation and reaction rate

Note: the process duration is 1 hour, temperature is 423 K.

We see from Table 2 that the rate of the reaction between adypic acid and polyethylene glycols is higher than that of the reaction between PRCG and PEG-400 and PEG-600. The reason is that PRCG is not a bifunctional compound in terms of the end carboxyl groups (see Table 1). Therefore, polycondensation degrees for polyesters obtained on the basis of PRCG and polyethylene glycols are lower than for the same glycols and adypic acid; see Fig. 3 and Table 2. The rate of polycondensation reactions actually does not depend on the molecular mass of the reagents. Polycondensation degrees of polyesters as well as their molecular masses depend only on molar concentration of carboxyl and hydroxyl groups in the reaction mixture, that is on functionality of the initial compounds.

During the polycondensation in the melt, as in any reversible reaction, the temperature affects the results in two ways. On one hand, the main reaction rate increases with the temperature increase. On the other hand, a temperature increase is the reason for the enhancement of side reactions, such as degradation and structure modification.

Given these two mutually opposite effects, we have studied effects of varying the temperature in order to establish the optimal temperature range. This was performed for the reaction of the petroleum resin with adypic acid and PEG-600. The catalyst was *p*-toluenosulphuric acid at the concentration of 1.2 mol %. The process temperature range was between 423 and 463 K. The results so obtained are shown in Figures 4–7.

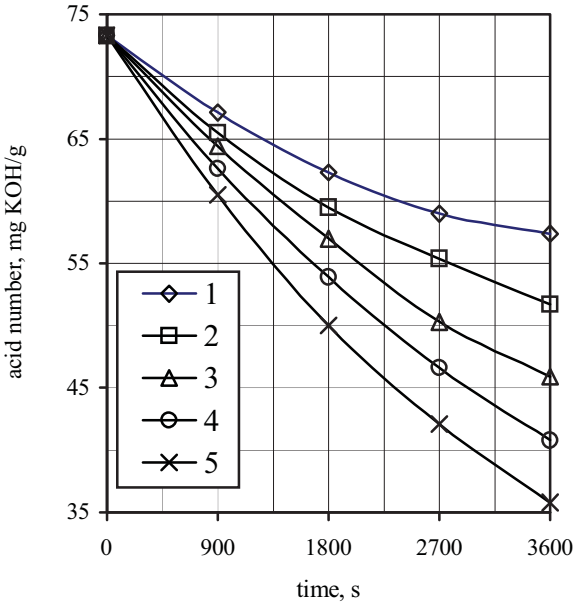

Fig. 4. Dependence of acid number on the reaction time for the reaction of the petroleum resin with the PEG-600 at different temperatures:
423 K (1), 433 K (2), 443 K (3), 453 K (4) and 463 K (5)

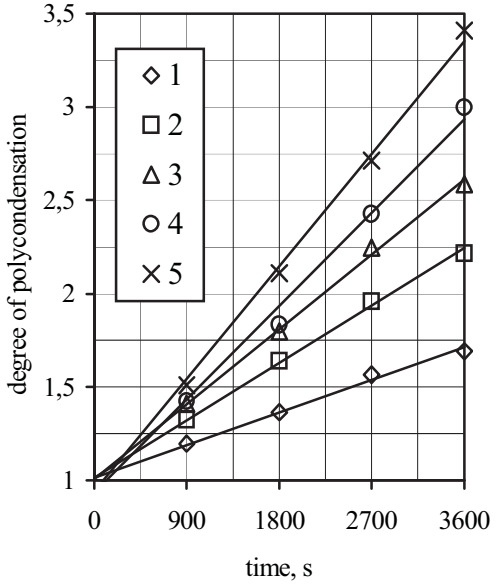

Fig. 5. Dependence of degree of polycondensation on the reaction time for the reaction of the petroleum resin with the PEG-600 at different temperatures: 423 K (1), 433 K (2), 443 K (3), 453 K (4) and 463 K (5)

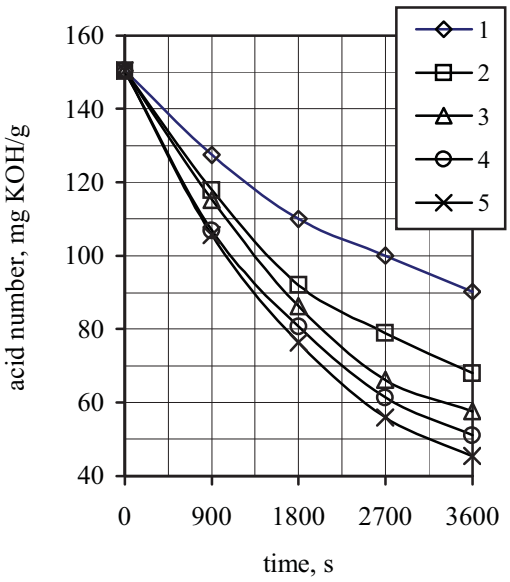

Fig. 6. Dependence of acid number on the reaction time for the polycondensation reaction between adypic acid and PEG-600 at different temperatures:
423 K (1), 433 K (2), 443 K (3), 453 K (4) and 463 K (5).

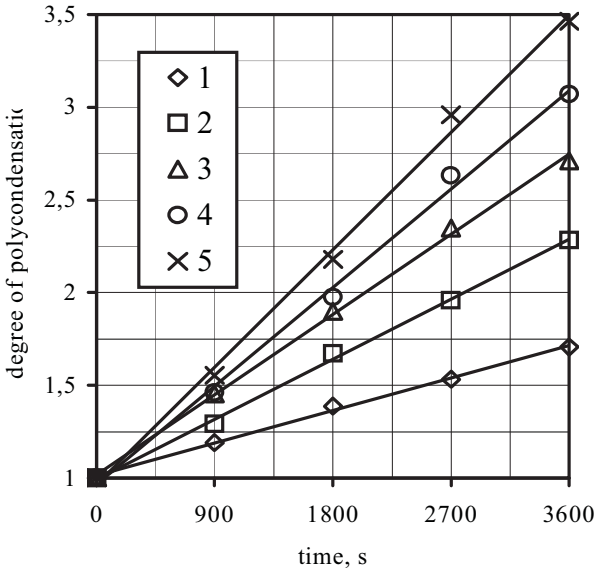

Fig. 7. Dependence of degree of polycondensation on the reaction time for the polycondensation reaction between adypic acid and PEG-600 at the different temperatures:
423 K (1), 433 K (2), 443 K (3), 453 K (4) and 463 K (5)

Degrees of polycondensation and effective rate constants have been calculated from the above results and are summarized in Table 3.

We find that the synthesis has to be started in the temperature range 423–428 K. The reasons are the physico-chemical characteristics of the reagents and polycondensation rate. The end synthesis temperature range has to be in the range 458–463 K to prevent polyethylene glycol evaporation and decomposition of dicarbonic acids; the dicarboxylation intensity increases with the temperature growth, especially in the presence of glycols.

Table 3

Effect of temperature on the reaction rate

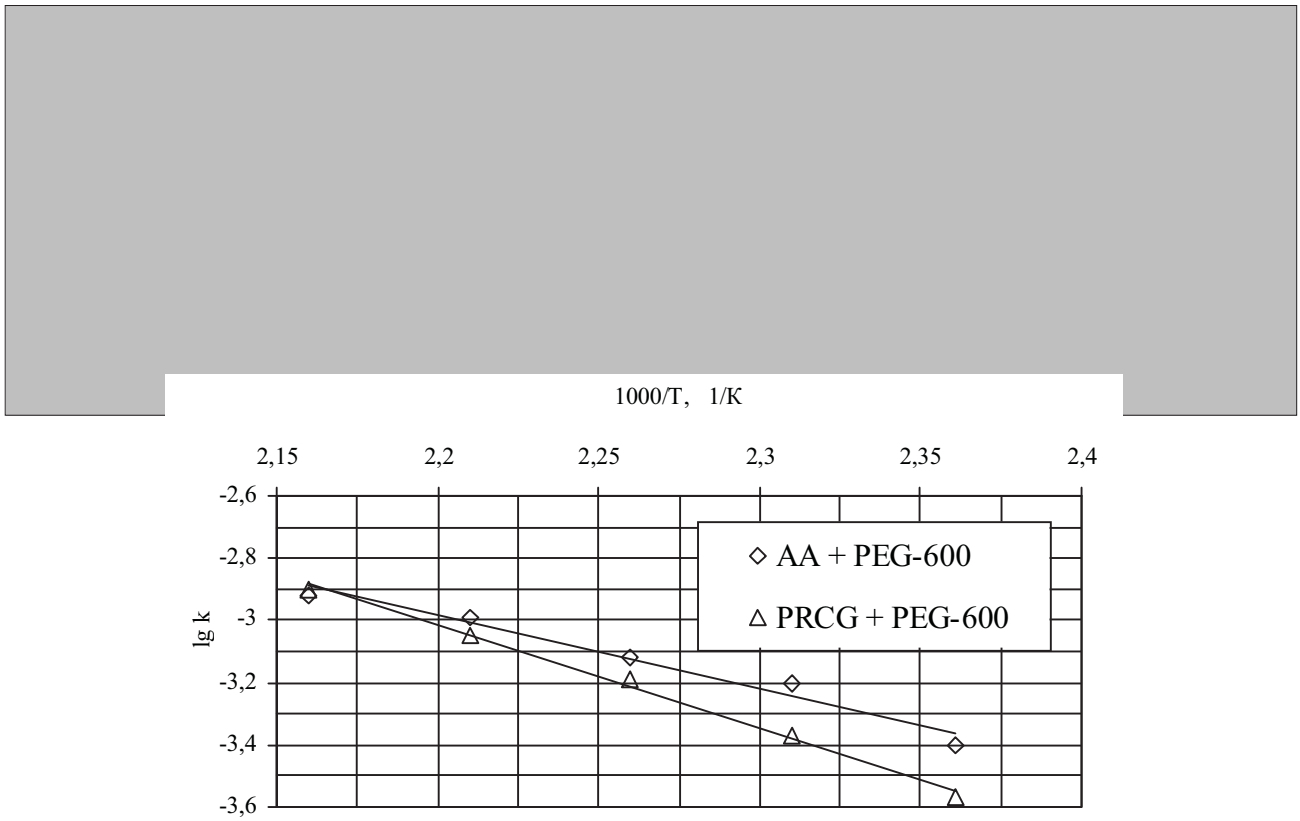

Fig. 8. Diagrams illustrating calculation of activation energies Ea for the polycondensation reactions

A well established and widely used procedure consists in expressing the effect of the temperature T on the reaction rate k_e by the so-called activation energy E_a determined from the Arrhenius equation:

$$\ln k = b - E_a/T. \quad (4)$$

For a discussion of Eq. (4) and its applications see for instance Kehlen, Kuschel and Sackmann [10]. As many others, we have used this equation before [11, 12]. We note in passing that a single equation describing the rate of progress of a reaction as a function of both temperature T and time t has been developed [13].

The results of using Eq. (4) are shown in Fig. 8. The linear character of the dependence of *log k* on *1/T* testifies to the fact that the change of rate constants with T is in agreement with the Arrhenius equation (4).

Calculated values of the activation energies E_a and temperature coefficient K_T are included in Table 3. They are typical for the most polycondensation reactions in the melt. Increase of K_T is connected with temperature increase indicating the increase of intensity of degradation processes taking place during polycondensation.

Thus, variation of temperature is a two-edged sword. Taking into account all pertinent factors, an optimized synthesis procedure of polyesters on the basis of petroleum resins and PE-I and PE-II polyethylene glycols has been developed.

4. Optimized Synthesis of Polyesters

PE-I polyester is obtained on the basis of PRCG and PEG-400. We take into the account that the resin functionality is 1.74 (see Table 1) and glycol functionality is 2. We load the reactor with 12.6 g (0.012 moles) of the resin and 4.0 g (0.01 moles) of polyethylene glycol.

The heating and stirring are switched on. Maintaining between 423 and 428 K, *p*-TSA catalyst in the amount of $2.38.10^{-2}$ g (1.2 mol % with respect to the acid component) is loaded into the reactor. The synthesis duration is 7 hours. For the first 1.5–2 hours the temperature is maintained at 433 K to decrease the possibility of glycol evaporation. Then the reaction mass is heated into the range 453–463 K. Polycondensation is carried out until completion of water formation. The change in the acid number is used additionally for a parallel control of the process.

Then the mixture is cooled down to 343–348 K. Toluene is added (50 ml) and the solution is transferred to a separation funnel. Distilled water (2–3 vol %) is added, the mixture is shaken up and than allowed to settle. The water layer is drained and the extraction is still repeated two more times. Toluene is distilled at vacuum.

A purified polyester is dried until a constant mass. The solid resin-like polyester is obtained in the amount of 14.8 g (the yield is 91.9 %). The color is dark brown. The polyester is soluble in toluene, acetone, dioxane and benzene (with heating).

PE-II polyester is synthesized on the basis of petroleum resin and PEG-600 analogously to the PE-I polyester. The difference is in the reagent mass. The quantity of the PRCG is 12.6 g (0.012 moles), PEG-600 - 6.0 g (0.01 moles) and *p*-TSA catalyst - 2.38.10-2 g (1.2 %). In this case the synthesis duration is 9 hours. The polyester is extracted by water from toluene solution. A solid resin-like polyester is obtained in the amount of 17.1 g (the yield is 93.7 %). The color is also dark brown. The polyester is soluble in toluene, acetone, dioxane and benzene (with heating).

A characteristic of the polyesters so synthesized is summarized in Table 4.

Table 4

Characteristics of polyesters obtained on the basis of petroleum resin and polyethylene glycols

Acknowledgments

Partial support of this work by the Robert A. Welch Foundation, Houston (Grant B-1203) is gratefully acknowledged.

References:

[1] Pratt G. and Smith M.: Polymer Internat., 2001, **51,** 21.
[2] Hess M. and Lopez B.: Ch. 9, [in:] W. Brostow (ed.), Mechanical and Thermophysical Properties of Polymer Liquid Crystals. Chapman & Hall, London 1998.
[3] Hess M.: High Performance Polymers, Ch. 21 [in:] W. Brostow (ed.), Performance of Plastics. Hanser, Munich - Cincinnati 2000.
[4] Hess M. and Pionteck J.: Mater. Res. Innovat., 2002, **6**, 51.
[5] Mano E.: Polimeros como materiais de engenharia. Edgard Blücher, Sao Paulo 1996.
[6] Feldman D.and Barbalata A.: Synthetic Polymers - Technology, Properties, Applications. Chapman & Hall, London 1996.
[7] Marais S., Hirata Y., Langevin D., Chappey C., Nguyen T.Q. and Metayer M.: Mater. Res. Innovat., 2002, **6**, 79.
[8] Bazyliak L., Bratychak M. and Brostow W.: Mater. Res. Innovat., 2000, **3**, 218.
[9] Bratychak M., Brostow W. and Donchak V.: Mater. Res. Innovat., 2002, **5**, 250.
[10] Kehlen H., Kuschel F. and Sackmann H.: Grundlagen der chemischen Kinetik, 3. berabeitete Auflage. Akademie-Verlag, Berlin 1996.
[11] Bratychak M., Bratychak M.M., Brostow W. and Shyshchak O.: Mater. Res. Innovat., 2002, **6**, 24.
[12] Bratychak M., Brostow W., Castano V., Donchak V. and Gargai H.: Mater. Res. Innovat., 2002, **6**, 153.
[13] Brostow W. and Glass N.: Mater. Res. Innovat., 2003, **7**, 125.

ПОЛІЕСТЕРИ НА ОСНОВІ НАФТОПОЛІМЕРНИХ СМОЛ І ПОЛІЕТИЛЕНГЛІКОЛІВ

Анотація. *На основі нафтополімерної смоли з карбоксильними групами і поліетиленгліколів одержані нові поліестери. Середня молекулярна маса нафтополімерних смол є 1050, функціональність 1,74. Для синтезу поліестерів оптимальним є еквімолярне співвідношення вихідних компонентів. Реакцію проводять у розчині в присутності пара-толуолсульфокислоти як каталізатора. При оптимальному температурному інтервалі 423–463 К вихід реакції становить 91–94 % і залежить від умов процесу. Швидкість реакції утворення поліестеру практично не залежить від довжини ланцюга молекул кислоти чи гліколю. Функціональність є головним чинником. Наведені ступені поліконденсації нових поліестерів.*

Ключові слова: *поліестер, смола, гліколі, поліконденсація, адипінова кислота, карбоксильна група*