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Cation-Exchange Fabric Prepared by Electron Beam-Induced Graft Copolymerization of Binary Monomer Mixture

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Summary: Applying the electron-beam preirradiation method in air the cation - exchange fabric (CEF) containing sulfonic acid (R-SO_3H) groups was prepared by graft copolymerization of sodium styrenesulfonate with acrylic acid onto non woven polypropylene fabric. The effect of reaction conditions on the grafting yield and reaction mechanism was examined.
The ion-exchange properties towards Cu(II) and Co(II) ions of the CEF were investigated depending on the form of the CEF and a pH of the solution. It was found that the synthesized CEF contains both strong acid groups (R-SO_3H) and weak acid (R-COOH) groups in almost equal proportion. The utilization of the CEF in Na^+ form allows to make the best use of its ion-exchange capacity.

Keywords: cation-exchange fabric; electron beam irradiation; preirradiation graft copolymerization; polypropylene fabric; sodium styrenesulfonate

Introduction

The production of sorption-active natural and synthetic fibers and textile materials is of great scientific and practical interest. This is determined by the fact that such kinds of materials, owing to their highly developed specific surface area and due to better ion-exchange and complexation parameters exhibit multiple advantages compared with synthetic ion-exchange resins and have gained great importance in solving of a wide range of ecological problems.

For the purpose of production such kind of materials the application of economical and ecologically clean radiation technologies is now under the intense attention of researchers.[1-3] In particular, the utilization of radiation-induced graft polymerization technique allows the modification of an inert polymeric matrix by grafting of a monomer with desirable functional group, or a precursor-monomer with subsequent chemical modification.

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For the practical purpose the production of strong acid cation-exchanger with sulfonate functional groups is an object of intense interest.[4,5] This work aims to synthesize the cation-exchange fabric with strong acid functional groups by means of radiation-induced graft copolymerization of acrylic acid and sodium styrenesulfonate onto nonwoven polypropylene fabric, to investigate the mechanism of binary monomer mixture graft copolymerization and to characterize cation-exchange properties of the resultant.

Experimental

Materials

Commercial nonwoven polypropylene fabric – PP - ($120 g/m^2$, degree of crystallinity of 65%, Toray-Saehan Co.Ltd) was used for grafting. Reagent grade acrylic acid -Aa- ($CH_2=CHCOOH$, Junsei Chemical Co.Ltd), sodium styrenesulfonate -SSS- ($CH_2=CHC_6H_4SO_3Na$, Tokyo Kasei Kogyo Co.Ltd), Mohr's salt ($(NH_4)_2Fe(SO_4)_2 \times 6H_2O$, Merck, Germany) were used as received.

Graft Copolymerization Procedure

Preirradiation grafting technique was employed for graft copolymerization of monomer mixture. Polypropylene fabric was irradiated in air at ambient temperature by an electron beam from an electron beam accelerator ELV-04 with accelerated energy of 1MeV for different time period.

After irradiation PP fabric was stored at room temperature in a dessicator. The irradiated fabric (about of 0.2 g) was weighted and immersed into a 100 ml glass flask with the monomer solution (Aa:SSS = 0.1M (7.2g) : 0.1M (20.6g) in 100 ml of water) and Mohr' salt additive. The flask was purged then by bubbling nitrogen, sealed up and placed in a water bath maintained at a constant temperature for different time periods. After the stipulated time period the grafted PP fabric was washed thoroughly with hot distilled water and methanol to remove homopolymers and unreacted monomer, dried in an oven at 50°C until constant weight was obtained.

The degree of cografting was calculated from the weight gain:

$$DG\% = [(W_1 - W_0)/W_0] \cdot 100$$

where W_0 and W_1 are the weight (g) of original and grafted fabric, respectively.

The preparation scheme is shown in Figure 1.

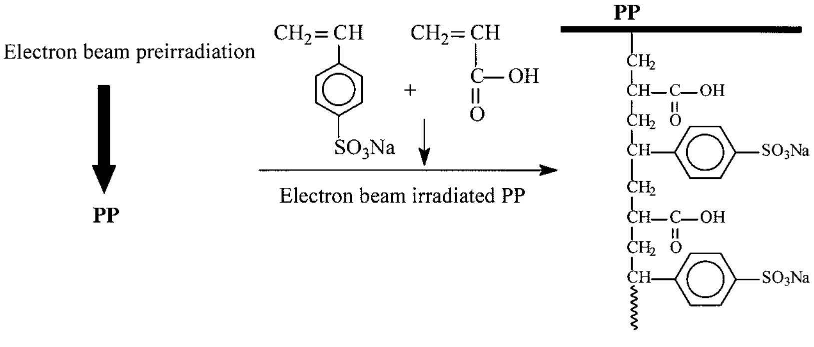

Fig. 1. Scheme of preparation of cation-exchange fabric by radiation-induced graft copolymerization of monomer mixture.

FT-IR Analysis

In order to confirm the introduction of functional groups onto PP fabric the IR spectra of modified fabric were obtained from FT-IR spectrometer (Perkin-Elmer, 1725).

Cation-exchange Capacity

Total cation-exchange capacity of the modified fabric, which reflects general content of acidic functional groups grafted onto PP trunk, was determined by backward titration experiments. For this purpose the grafted PP fabric (about 0.2g) was completely converted to the H^+ form by treatment with excess solution of 0.1M HCl for 12h. The sample was than washed with water to remove sorbed HCl, until the washing solution became neutral and dried at 60° C to a constant weigh. Subsequently the H^+ form sample was weighted and put into a flask with 0.20 ml of standard 0.5M NaOH solution stoppered down and shaken for about 12h. After shaking, 2ml aliquots of the solution was titrated to the phenolphthalein end point with standard 0.1 M HCl solution.

To separate the contribution to the total cation-exchange capacity of both carboxylic and sulfonic acid groups a set of kinetic-exchange experiments depending on the form (H^+- or Na^+) and a pH of the solution was carried out.

Me(II) Ions Exchange Capacity

The rate of exchange of Cu(II) and Co(II) ions from Me(II)-ion solutions with different pH (at 4 and 8) was determined by contacting about of 0.2 g modified PP fabric with 50 ml Me(II)-ion solution at 22°C under stirring (140 rpm). 1 ml solution was collected at appropriate time intervals for metal-ion determination by using of atomic absorption spectroscopy with wavelength set at 324.8 nm for Cu and 240.7 nm for Co (AA-spectrophotometer, Model UNICAM 989, England).

The quantities of metal ions adsorbed per unit of dry weight of the CEF (mg/g) were calculated by the following expression:

Metal ions adsorbed = $(C_0\text{-}C)\ V/W$

Where, C_0 and C are the Me(II)-ion concentrations in the Me(II)-ion solution before and after the incubation period, respectively (mg/ml); V is the volume of the solution (ml); W is the weight of the adsorbent used (g).

Results and Discussion

Copolymerization Process

Strong acid cation exchanger was prepared by radiation-induced graft copolymerization of acrylic acid and sodium styrenesulfonate monomers onto PP fabric. We, like other investigators,[6] were unable to graft SSS monomer onto PP fabric from water solution, but copolymerization of SSS with Aa occurred successfully. Many factors affect the radiation grafting process of binary monomer mixture. Among them, investigated here, are total exposure dose, reaction time and temperature, concentration of specific additives (Mohr's salt). The effects of these factors has been evaluated from the viewpoint of obtaining cation-exchange fabric with reasonable grafting degree.

When polypropylene fabric is irradiated in the presence of air, mainly hydroperoxides are formed onto the polymeric backbone. These hydroperoxides decompose upon heating to generate hydroxyl radical ($OH^{\cdot}$) and the macroradical ($PPO^{\cdot}$). The macroradical offers a site for grafting, while the hydroxyl radical initiates the polymerization of a monomer (homopolymerization). The various processes occurring during the irradiation and grafting reaction may be outlined as follows:[7]

$$\mathrm{PP\text{-}H} \xrightarrow{O_2} \mathrm{PP\text{-}OOH} \xrightarrow{HEAT} \mathrm{PPO^{\cdot}} + \mathrm{OH^{\cdot}}$$

$$\mathrm{PPO^{\cdot}} + \mathrm{nM} \rightarrow \mathrm{PPO\text{-}\,M^{\cdot}_{n}}$$

$$\mathrm{M} + \mathrm{OH^{\cdot}} \rightarrow \mathrm{M^{\cdot}\text{-}OH} \xrightarrow{nM} \mathrm{M^{\cdot}\text{-}(M)_{n}\text{-}OH}$$

$$\mathrm{PPO^{\cdot}} + \mathrm{M^{\cdot}\text{-}(M)_{n}\text{-}OH} \rightarrow \mathrm{PPO\text{-}\,M\text{-}(M)_{n}\text{-}OH}$$

It can be seen that the hydroxyl radical can initiate undesirable homopolymerization, that leads to lower grafting yield. To overcome homopolymerization some small amount of a transition metal salt is usually used as an inhibitor:[8,9]

$$\mathrm{OH^{\cdot}} + \mathrm{Fe^{2+}} \rightarrow \mathrm{OH^{-}} + \mathrm{Fe^{3+}}$$

In our case, no homopolymer formation was observed in the reaction medium at the reaction temperature 50°C. The degree of monomer mixture grafting onto PP fabric during the reaction time of 12 h reached only 19%, while the addition of small amount of Morh's salt to the reaction medium leaded to a significant increase of grafting. Apparently, it is connected with well known fact, that transition metal ions favour the decomposition of the hydroperoxides:

$$\mathrm{PP\text{-}OOH} + \mathrm{Fe^{2+}} \rightarrow \mathrm{PPO^{\cdot}} + \mathrm{OH^{-}} + \mathrm{Fe^{3+}},$$

The excessive adding of metallic salt may cause a deactivation process and lead to the decrease of grafting yield:

$$\mathrm{PPO^{\cdot}} + \mathrm{Fe^{2+}} \rightarrow \mathrm{PPO^{-}} + \mathrm{Fe^{3+}}$$

The influence of Mohr's salt concentration on the degree of graft copolymerization of Aa and SSS monomer mixture was studied and the results are presented in Table 1. It can be seen that the addition of Mohr's salt to the reaction medium exhibits an increasing trend of grafting yield up to the maximum value at 10^{-3} w% of Mohr's salt content. It should be noted that the trend of the influence of Mohr's salt content onto degree of the monomer mixture grafting is quite similar to that when only acrylic acid has been grafted under the same experimental conditions.

The effect of absorbed dose on the monomer mixture grafting is presented in Figure 2. It is observed that the degree of grafting increases slowly up to 40.3 kGy, and then begins to rise significantly up to 70.5 kGy. In the IR spectra of grafted samples, irradiated with doses less than 40.3 kGy, only a characteristic band at 1708 $\mathrm{cm^{-1}}$ assigned to -C=O group of acrylic acid was observed, while the IR spectra of the samples, irradiated with higher doses, exhibited also characteristic absorption bands attributed to SSS group.

Table 1. Effect of Mohr's salt concentration on the degree of graft copolymerization.

Content of Mohr's salt, w%	Degree of grafting	
	SSS+Aa monomer mixture*	7% Aa
0	18.6	57.7
5×10^{-5}		61.7
10^{-4}	29.3	113.0
5×10^{-4}	86.5	150.4
10^{-3}	110.0	164.6
5×10^{-3}	82.2	108.3
10^{-2}	79.7	101.4
10^{-1}	19.9	34

Reaction conditions: Absorbed dose-70.5 kGy; reaction temperature–50°C; reaction time – 12h.
*Monomer mixture consists of 0.1M SSS (20.6g): 0.1M Aa (7.2g) in 100ml H_2O

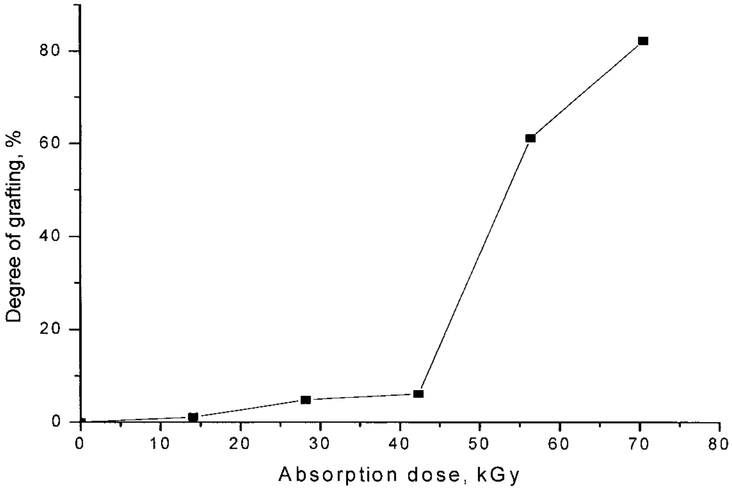

Fig. 2. Effect of absorbed dose on the on the degree of graft copolymerization of Aa-SSS monomer mixture (reaction temperature–50°C; reaction time-12h; 10^{-2} w% Mohr's salt additive).

In order to clarify the mechanism of graft copolymerization of the monomer mixture the kinetic curve of grafting at 50°C as well as corresponding IR spectra were investigated. It can be seen from Figure 3 that the kinetic curve of graft copolymerization consists of different stages (within 0-9 h; 9-12 h, 12-33 h), that probably may reflect the phased development of cografting process. At the first stage (0-9 h) of the kinetic curve, a slow increase of the copolymerization rate occurs, while the second stage (9-12 h) is characterized by an intensive growth of the copolymerization rate, after which there is a slowing down on the following stage (12-30 h), reaching a saturation at 28-32 h.

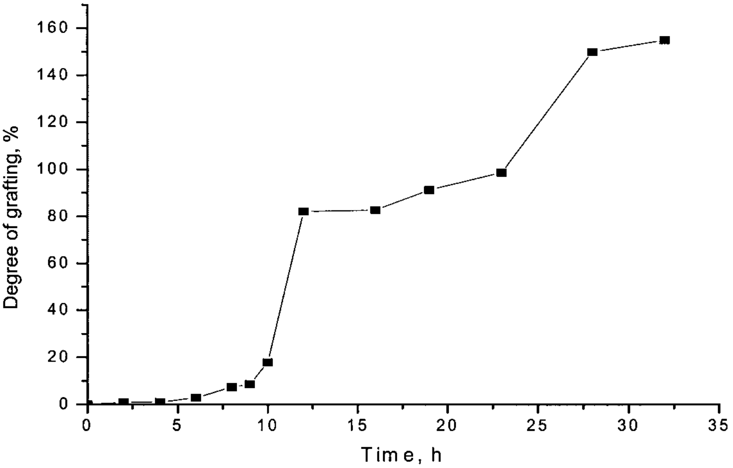

Fig. 3. Kinetic curve of graft copolymerization of Aa-SSS monomer mixture (70.5 kGy absorbed dose; 50°C reaction temperature; 10^{-2} w% Mohr's salt additive).

Figure 4 shows the IR spectra of the samples of appropriate stages. It can be seen that the IR spectra of the first stage (2,9%, 7.3%, 8.6, 17.8) exhibit only the absorption band at 1715 cm^{-1} due to carbonyl group (-C=O) of acrylic acid. As the intensity of this absorption band extends with the increase of grafting degree, so these data testify that the kinetic curve at this stage reflects the peculiarity of grafting of acrylic acid. The characteristic absorption bands of sulfonic acid group {1150 cm^{-1} (asymmetric stretch), 1030 cm^{-1} (symmetric stretch), 670 cm^{-1}} appear in the IR spectra of the subsequent stages. Their intensity extends with the increase of grafting degree, as well as the intensity of carbonyl absorption band.

These data confirmed our assumption about stepwise development of copolymerization process and allowed us to judge about its mechanism. The process begins with the grafting of acrylic acid monomers onto PP backbone (at the first stage) and goes on after that by the inclusion of the SSS monomers into the growing chains.

The maximal degree of grafting (155%) was obtained under the following conditions – absorbed dose 70.5 KGy, reaction temperature 50°C and reaction time 32h.

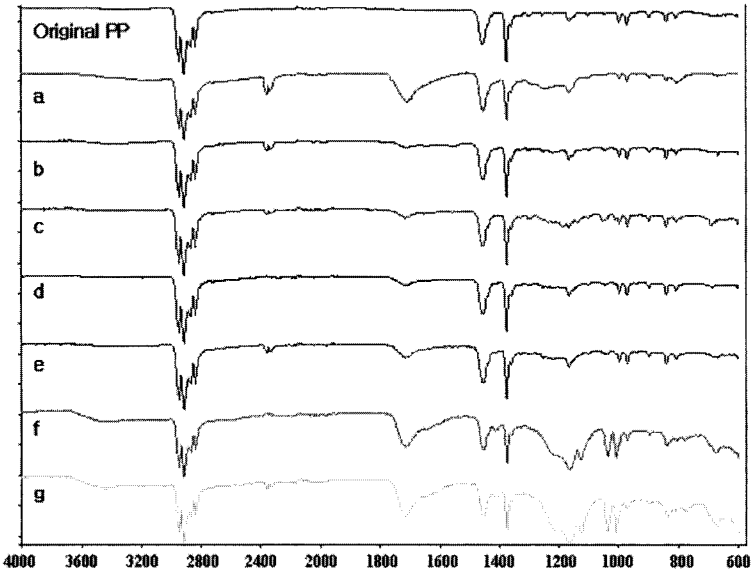

Fig. 4. IR-spectra of original polypropylene fabric (PP); (a) acrylic acid grafted PP fabric (DG=95%); (b-g) Aa-SSS monomer mixture grafted PP fabric with DG=2.9%; 7.7%; 8.8%; 17.8%; 82.6%; 98.6%, respectively. Reaction conditions: absorbed dose: 70.5 kGy; reaction temperature: 50°C.

Cation-exchange Properties

As a result of radiation-induced graft copolymerization of sodium styrene sulfonate and acrylic acid onto PP fabric the cation–exchanger was obtained. The main specificity of the synthesized CEF is that it represents a bifunctional cation-exchanger, carrying two types of functional groups

– both week acid and strong acid ones and strictly speaking can't be classified as strong acid – or week acid cation-exchanger. Strong acid exchanger are so named because their chemical behaviour similar to that of a strong acid: it is highly ionizied in both the acid (R-SO_3H) and salt (R-SO_3Na) form; its hydrogen and sodium forms are highly dissociated and the exchangeable Na^+ and H^+ are readily available for exchange over the entire pH range. So the exchange capacity of strong acid cation-exchanger is independent of a solution pH. In a week acid cation-exchanger the ionizable group is a carboxylic acid group, so that it behaves similarly to weak organic acids in that the degree of dissociation is strongly influenced by pH. As a rule it has limited capacity below a pH of 6.0.

As the cation-exchanger considered here is a bifunctional cation-exchanger it follows as a logical consequence that its behaviour will depend on a solution pH therefore for its practical application the evaluation of the content of both strong (sulfonic) and weak (carboxylic) acid groups would be extremely important.

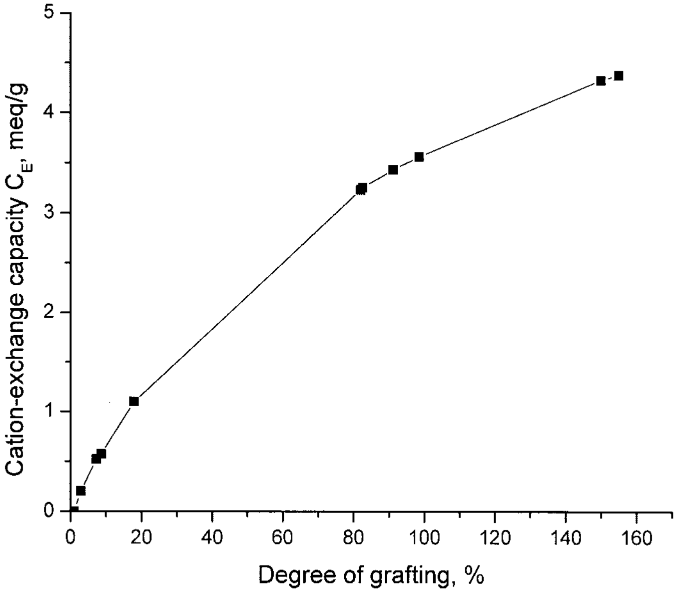

Fig. 5. Dependence of the total cation-exchange capacity of Aa-SSS grafted fabric upon the degree of graft copolymerization.

The total exchange capacity of the synthesized CEF, which reflects the total content of acidic functional groups (both carboxylic and sulfonic), has been determined by backward titration method. A relationship between the total cation exchange capacity of the CEF and the degree of graft copolymerization is shown in Figure 5. Maximum value of the total exchange capacity of 4.30 meq/g was obtained for the CEF with 155% grafting degree.

To determine the separate contribution of each of two acidic functional groups to the total exchange capacity a number of experiments in binding of Cu(II) and Co(II) ions from the acidic solutions (pH=4) were carried out. The equilibrium value of Me(II) ions binding capacity measured in acidic solution allows us to determine the amount of strong acid (sulfonic acid) functional groups, owing to weak dissociating of the carboxylic groups and unavailability of their hydrogen ions for exchange in acidic solution. Subsequently, taking into account a value of total exchange capacity we can easily calculate the amount of carboxylic groups.

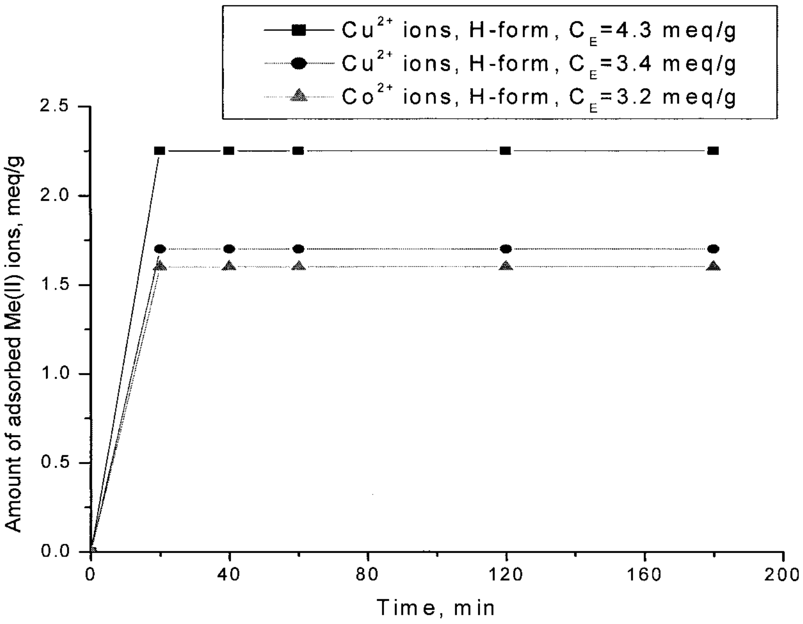

Fig. 6. Sorption rates of Me(II) ions on the Aa-SSS grafted fabric samples in H-form with different values of the total exchange capacity from acidic solution (pH=4).

Three samples of the synthesized CEF in the H^+ form with value of total exchange capacity of 3.2 meq/g, 3.4 and 4.3 meq/g were taken for the experiments of Me(II) ions binding from acidic solution. The kinetic curves of Cu (II) and Co(II) ions sorption from acidic solution on the synthesized CEF in the H^+ form are presented in Figure 6. It can be seen that the adsorption capacity of the investigated samples was two times lower than their total exchange capacity (1.55 meq/g, 1.68 and 2.25 meq/g, correspondingly). It means as a logical consequence that the CEF obtained by radiation-induced graft copolymerization of sodium styrenesulfonate and acrylic acid contains groups of strong acid (R-SO3H) and weak acid (R-COOH) in almost equal proportion. Figure 7 shows the adsorption rate of Co(II) ions from basic solution (pH=7.8) on the CEF in Na^+ form with total exchange capacity of 3.6 meq/g. As seen here, the cobalt adsorption capacity increases with the time during the first 20 min and then levels off towards the equilibrium adsorption capacity of 3.67 meq/g. Thus, the application of grafted fabric in Na^+ form in basic solution allows to utilize its total exchange capacity completely.

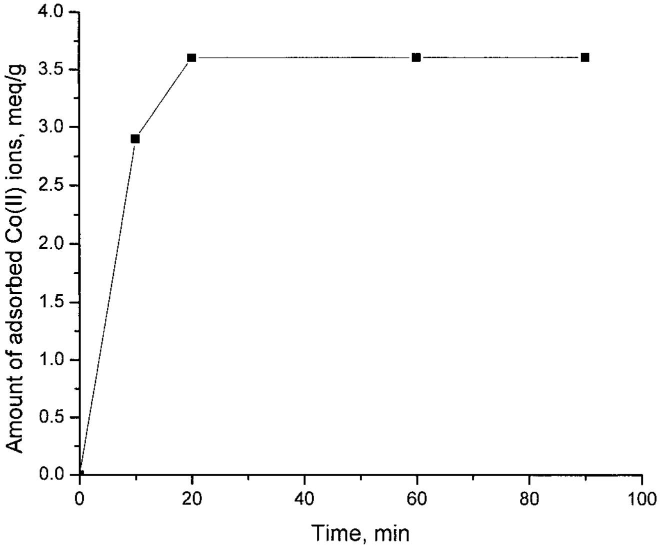

Fig. 7. Sorption rates of Co(II) ions on the AA-SSS grafted fabric in Na-form from basic solution.

Conclusions

Cation–exchange PP fabric with strong acid (R-SO_3H) groups has been prepared by radiation-induced graft copolymerization of binary monomer mixture, consisting of sodium styrene sulfonate and acrylic acid, onto nonwoven PP fabric. The main factors affecting the radiation grafting process of binary monomer mixture onto PP fabric have been considered. Comparing the kinetic curve of graft copolymerization of Aa-SSS monomer mixture at 50°C with the IR spectra of the appropriate samples a scheme of graft copolymerization process has been proposed. The process begins with the grafting of acrylic acid monomers onto PP backbone, followed by the inclusion of the SSS monomers into the growing chains.

The total exchange capacity of the grafted fabric versus its grafting degree has been evaluated. The investigation of the synthesized CEF's ion-exchange capacity in the acidic solutions towards Cu(II) and Co(II) ions allowed us to make a conclusion that the CEF contains groups of strong (R-SO3H) and weak (R-COOH) acid in almost equal proportion and consequently it exhibits strong acid behaviour over the entire pH range in half of its total exchange capacity. The application of the CEF in Na^+ form in basic solution allows to utilize its total exchange capacity completely.

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