Polypropylene membranes with the double sensitivity effect

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ABSTRACT: This article describes the modification of polypropylene membranes leading to the preparation of thermo- and pH-sensitive structures. Poly(N-isopropylacrylamide), poly(acrylic acid), or copolymer poly(N-isopropylacrylamide-co-acrylic acid) was grafted on to the membranes' surface activated by dielectric barrier discharge plasma. The properties of the modified membranes were evaluated by means of infrared spectroscopy and contact angle measurements. The effect of modification was monitored by the determination of water flux at two temperatures (20 and 45°C) and at various pH values (2.8–8.0). The membrane separation properties were investigated for the solutions of o-bromocresol purple. It was found that membranes grafted with copolymer were responsive to both stimuli and they could be used for separation purpose. The separation performance was tailored by alteration of pH and temperature of feed solution. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41763.

INTRODUCTION

The growing development of membrane techniques enforces search for new membranes designed for more efficient processes. Since the beginning of the 1960s of the previous century, the development of membranology has been related to the availability of polymers on the market.[1] Unfortunately, a large-scale production of new polymers has not been commercialized for the last two decades and it is not expected that such technology will be launched soon.[2] Such situation has enforced the search for some alternative methods that allow tailoring new membranes. They have been developed in two directions: (i) to modify basic polymer and to prepare the membrane from derivative(s) and (ii) to prepare membrane according to the standard procedures followed by membrane modification. It is obvious that the second approach is faster and more versatile. It can be carried out by chemical and plasma activation of membranes that are subjected to surface grafting.[3,4]

Owing to a fast, effective, and ecologically friendly action, plasma is considered to be a promising tool for surface modification. Plasma is a gaseous mixture of electrons, charged ions, and neutral atoms or molecules that, in contact with solid matter, can activate the surface groups to form some graft-anchoring sites.[5] The effect of the modification depends on the type of gas used for the process. Among various gases, the following are most frequently applied: oxygen, argon, nitrogen, air, water, and carbon dioxide.[6] This method is the subject of this article.

One of the most interesting applications of plasma for the alteration of membrane properties is grafting of polymer brushes. When the grafted polymers show dual response to external stimuli, the obtained membrane becomes more versatile for process engineers. According to the definition proposed by Wee and Bai,[7] stimuli-responsive membranes are defined as engineered interfaces that would behave responsively and reversibly of which the barrier properties (selectivity and permeability) and interfacial properties (wettability and polarity) are controllable by manipulating the membrane environment. When a suitable impulse acts, independently of its nature: physical, chemical, or biological,[8–10] the grafted chains change their shape and these changes alter the character of the surface. So far, only few "smart polymers" were grafted on surfaces and used as new kind of membranes.[11–13]

Poly(N-isopropylacrylamide) (PNIPAM) is one of the best recognized temperature-responsive polymers. At a temperature lower than 32°C, water behaves as a good solvent and PNIPAM chains are fully strengthened. When temperature rises above 32°C, the PNIPAM chains collapse. In the case of chains grafted on a surface, the "coil-to-globule" transition causes the alteration of surface character from a hydrophilic to a more hydrophobic one. Polyelectrolytes belong to the pH-sensitive group of responsive polymers. Their chains swell or collapse in response to the pH value of the surrounding media. The best example of polyelectrolyte is poly(acrylic acid) (PAA) turning to polyanion at a pH value of >4.7. The carboxyl groups of PAA release H^+

Table I. The Variables for the Grafting Process

	AA	NIPAM	AA : NIPAM 2 : 1	AA : NIPAM 1 : 1	AA : NIPAM 1 : 2
Solution concentration (vol. %)	30	30	20 : 10	15 : 15	10 : 20
UV time (min)	2-5	8-14	4-8.50	5-7.40	5-10

ions and convert to —COO⁻ groups that are better hydrated. Again, when the chains are fixed to a surface, the pH alteration causes the change of surface character.

The above-described phenomena were used to build new types of reverse osmosis membranes resistant to hydrophobic foulants with improved water permeability and enhanced cleaning efficiency.[14,15] To meet the requested properties, two stimuli-responsive polymers, PNIPAM and PAA, were grafted to membrane surface. They had different roles: polyacrylamide reduced fouling as well as improved cleaning properties and PAA increased water flux through membrane.

Yamaguchi[16–18] described another phenomenon related to the presence of smart polymer chains on the surface of a porous membrane. In some conditions, the diameter of the membrane pores varies. In consequence, the permeability of such membranes changes in respect to the external conditions. This phenomenon allows to develop tunable membranes for the separation of multicomponent mixtures.[19] As the example, the properties of polypropylene membrane grafted with copolymer of PNIPAM and PAA[20] could be taken. It was found that the water flux through the modified membranes was sensitive either to the solution's pH or to the temperature.

The aim of this study was to evaluate the properties of multistimuli-responsive membranes and to quantify the effects introduced by the grafted polymers. To obtain brush-like membranes, the dielectric barrier discharge plasma was applied for grafting PAA, PNIPAM, or copolymer of acrylic acid-N-isopropylacrylamide to the surface of the porous polypropylene (PP) membranes. By such approach, new kinds of membranes were obtained and evaluated for filtration properties related to both external stimuli: pH value and temperature.

EXPERIMENTAL

Materials
PP membrane (Hoechst Celgard Corporation; pore size: 0.2 μm, porosity: 60%, and thickness: 25.4 μm) was used as the polymer support.

N-isopropylacrylamide (NIPAM, Sigma Aldrich) and acrylic acid (AA, Merck) were used as functional monomers. NIPAM was recrystallized from n-hexane, whereas AA was used as delivered.

Plasma Treatment
A dielectric barrier discharge plasma device (Dora Power Sys., Poland) was applied to activate the polypropylene membrane. The plasma parameters (voltage, 20 kV; current, 5 mA; argon flow, 20 L/h; modification time, 60 s) were kept constant during the whole study.

Grafting Procedure
The sample of membrane was placed into a plasma reactor and treated with dielectric discharge plasma on both sides. After the treatment, the sample was kept in the air for 10 min, immersed in aqueous solution of monomers (AA or NIPAM, or mixtures of both monomers), and irradiated with UV lamp (2 kW). The parameters of grafting are listed in Table I. To remove the unbound polymers, the samples were washed with a large amount of distilled water.

Characterization of Modified Membranes
Grafting Yield. The grafting yield, expressed in mg/cm², was calculated according to eq. (1):

$$GY = \frac{M_1 - M_2}{A} \qquad (1)$$

where M_1 and M_2 are the weights of membrane after and before grafting (mg); A is the membrane area (cm²).

Infrared Spectroscopy. To characterize the modified membranes, the infrared (IR) spectra were collected by means of Perkin-Elmer System 2000 with 64 scans of 4 cm⁻¹ resolution each. The ATR device equipped with Ge crystal of 45° angle was used.

Scanning Electron Microscopy. The morphology of membrane surface was investigated by SEM microscope Carl Zeiss EVO LS15 operated at 5.00 and 10.00 kV. Prior microscopy evaluation, the surface was sputter coated with gold.

Contact Angle and Surface Energy. Dynamic contact angles of water, diiodomethane, and formamide were measured by goniometer PG-X (Fibro Systems). The measurements were carried out on both neat and modified membranes. Total surface energy of samples (γ) as well as its acid–base (γ^{AB}) and dispersive (γ^{D}) components was calculated according to the harmonic averaging protocol. The surface polarity was calculated as the contribution of acid–base component to the total surface energy according to eq. (2):

$$P = \left(\frac{\gamma^{AB}}{\gamma}\right) \times 100\% \qquad (2)$$

Water Permeability. Water permeability through evaluated membranes was tested at pH = 3.0 or 5.5, and at 20 or 45°C. The pressure in Amicon 8050 cell was set to 0.05 MPa. Prior to filtration measurements, membranes were hydrophilized by immersion in ethanol (30 min) followed by transfer to pure water.

**Average Pore Size.** Pore sizes, r (μm), were calculated according to eq. (3):
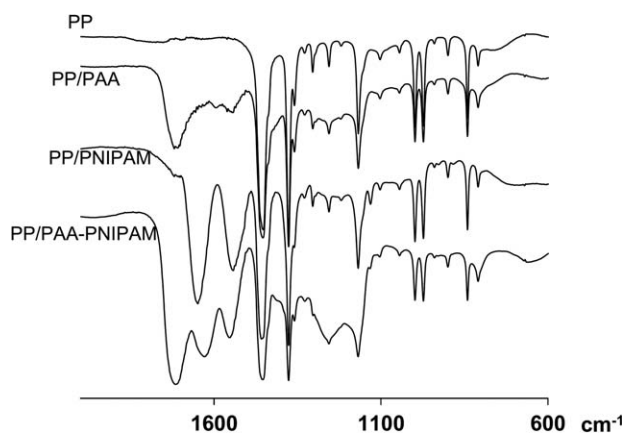
Figure 1. IR spectroscopy, PP: nonmodified membrane, PP/PAA: membrane grafted by PAA, PP/PAA: membrane grafted by PAA, PP/PNIPAM: membrane grafted by PNIPAM, PP/PAA-PNIPAM: membrane grafted by PAA-PNIPAM (monomers ratio, AA : NIPAM 1 : 2).

$$r = \sqrt{\frac{8Jd\eta}{p\varepsilon}} \qquad (3)$$

where J is water flux (L/m^{2}h), d is membrane's thickness (m), η is water's viscosity (Pa s), p is pressure (Pa), and ε is membrane porosity ($g_{H2O}/g_{dry\ membrane}$).

Effect of Temperature and pH on Volumetric Flux. Water permeability was measured at 45 or 20°C for solutions with pH of 3.0 or 5.5. The tested membrane was hydrophilized and stored in appropriate solution before taking measurements. The equilibrated membrane was fixed in the Amicon 8050 cell and cell was filled with suitable aqueous solution, kept for 20 min to equilibrate the whole system and pressurized to 0.05 MPa. In the case of evaluation of kinetics of flux change, the system was not equilibrated. Once the membrane flux reached the steady-state value, the flux was measured in triplicates by recording the volume of permeate collected in the given time intervals.

Separation Properties. The Separation properties were investigated for membranes with the grafting yield of about 0.1 mg/cm^2. Water flux was determined for the solutions whose pH values
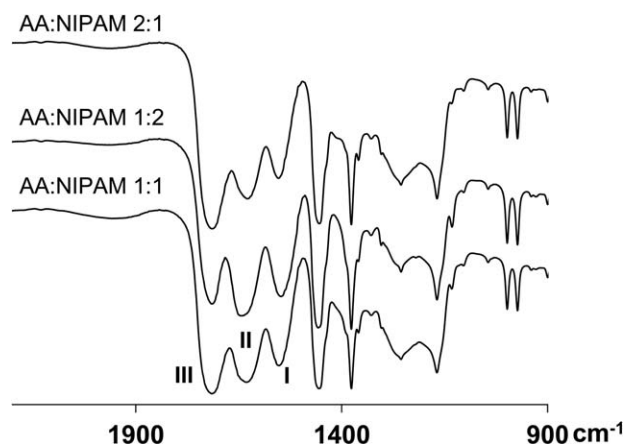
Figure 2. IR spectroscopy, PP membrane grafted by PAA : PNIPAM: AA : NIPAM 2 : 1 monomer ratio 2 : 1, AA : NIPAM 1 : 2 monomer ratio 1 : 2, AA : NIPAM 1 : 1 monomer ratio 1 : 1.
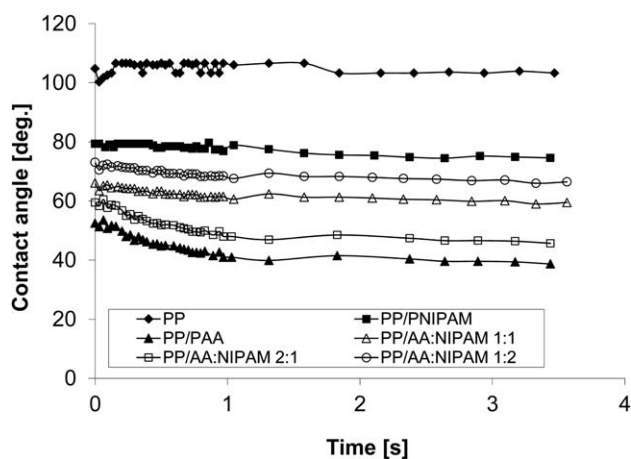
**Figure 3.** The dynamic water contact angle of modified membranes.
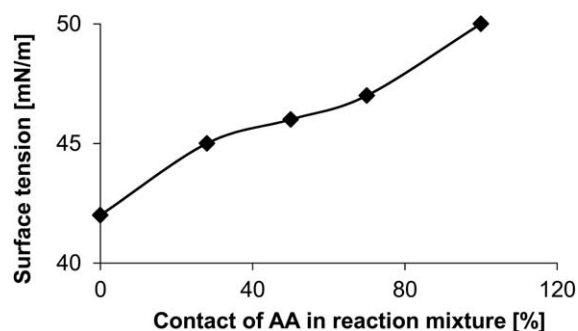
Figure 4. The surface energy in relation to monomer being used for grafting. PP membrane $\gamma = 30.6$ mN/m.

were changed and at 20 or 45°C. The membranes were tested for the rejection of *o*-bromocresol purple (BP). The dye solution of 1.0 mg/L of BP was placed into the Amicon 8050 cell and equilibrated at 20 or 45°C within 20 min. The pH value of solution was set at 3.0, 5.25, or 6.5. All experiments were conducted at a pressure of 0.05 MPa and were triplicated. The concentration of BP in the permeate was detected spectrophotometrically at 430 nm for pH values of 3.0 and 5.25, and at 590 nm for pH value of 6.5. The solute rejection (R) was calculated according to eq. (4).

$$R = \left(1 - \frac{C_p}{C_0}\right) \times 100\% \qquad (4)$$

where C_p is the concentration of BP in permeate (mg/L) and C_0 is the concentration of BP at the beginning (mg/L).
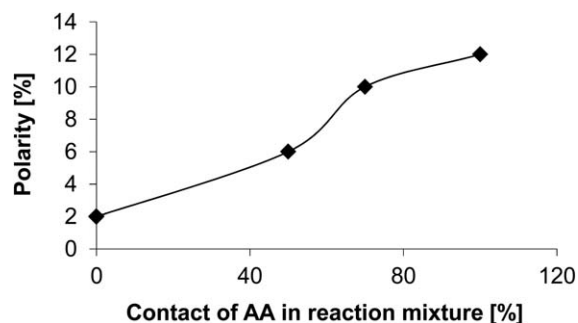
Figure 5. The surface polarity of grafted membranes. The effect of acrylic acid content. PP membrane $P = 1.9\%$.

RESULTS AND DISCUSSION

One of the simplest methods for the preparation of stimuli-responsive membranes is grafting of smart polymers onto the surface of porous membrane. To follow the effect of modification, the properties of grafted membranes were evaluated by means of IR spectroscopy, scanning electron microscopy (SEM), and contact angle measurements.

IR spectroscopy allowed to characterize the chemical composition of the modified membranes. Figure 1 shows IR spectra of a nonmodified PP membrane, membrane grafted with PP/PAA,
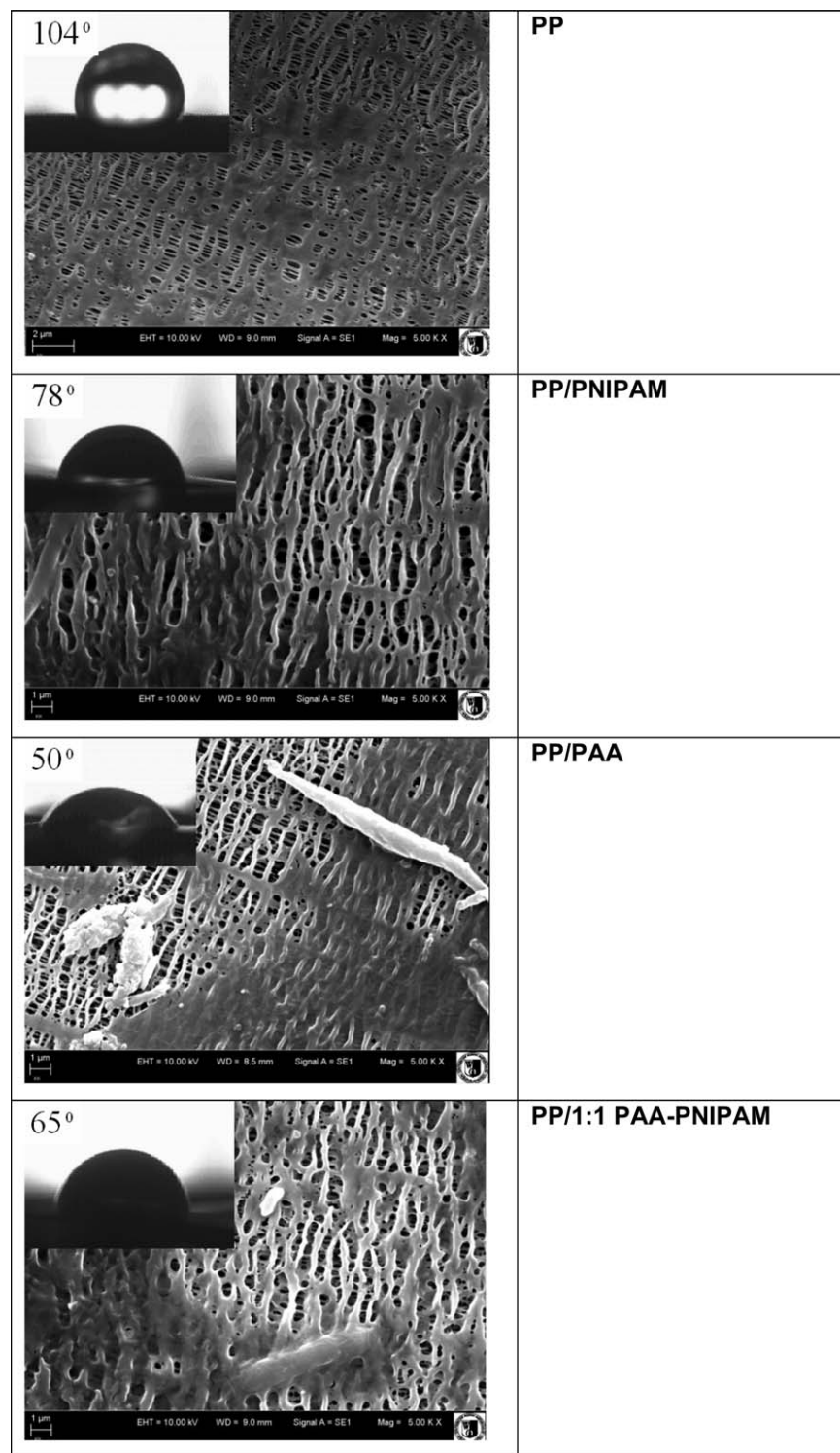

Figure 6. The SEM images of modified membranes.

Table II. The Average Pore Size versus Grafting Yield ($P = 0.02$ MPa)

Membranes	GY (mg/cm^2)	r (µm)			
		pH = 3.0	pH = 5.5	20°C	45°C
PP	0	0.24	0.24	0.24	0.240
PP/PNIPAM	0.174	0	0	0	0.220
	0.436	0	0	0	0.017
	1.258	0	0	0	0.008
PP/PAA	0.169	0.221	0	0	0.190
	0.445	0.017	0	0	0.016
	1.133	0.008	0	0	0.007
PP/PAA-PNIPAM 1 : 1	0.194	0.222	0	0	0.211
	0.452	0.013	0	0	0.016
	1.084	0.009	0	0	0.009
PP/PAA-PNIPAM 2 : 1	0.142	0.222	0	0	0.204
	0.413	0.014	0	0	0.012
	1.171	0.009	0	0	0.007
PP/PAA-PNIPAM 1 : 2	0.152	0.216	0	0	0.221
	0.482	0.018	0	0	0.018
	1.304	0.009	0	0	0.009

with PNIPAM, PP/PNIPAM, and with copolymer PP/P(AA-*co*-NIPAM).

In the spectrum of PP/PAA membrane, the absorption band at 1707 cm^{-1} attributed to C=O stretching bending was observed. Additionally, the peaks at 1640 and 1550 cm^{-1} showed the presence of C(O)OH groups. These bands confirmed that PAA chains were grafted to membrane surface. In the case of membranes grafted with PNIPAM chains, the peaks at 1540 and 1650 cm^{-1} were attributed to the band of N—H and C=O groups, respectively. In the IR spectra of PP/PAA-PNIPAM 2 : 1, the band at 1620 cm^{-1}, related to N—H groups of PNIPAM, was observed. In addition, the wide peak at 1705 cm^{-1} confirmed the presence of carboxylic acid in the grafted copolymer. The obtained data were consistent with spectra described in Ref. 15 and confirmed that the membranes were modified successfully.

Figure 2 shows the analysis of membranes grafted with copolymers AA : NIPAM 2 : 1, 1 : 2, and 1 : 1, respectively. There were three absorption bands characteristic to both polymers: PAA and PNIPAM. The absorption band "I" indicated the presence of C(O)O groups of PAA and C=O groups of PNIPAM. The band "II" was typical for N—H groups of PNIPAM, whereas the band "III" for C=O groups of PAA. In IR spectrum of a membrane modified with monomer mixture with a larger amount of AA, the "I" band intensity was higher than the intensity of the "II" band. In the opposite situation, when NIPAM concentration exceeded the AA concentration, the intensity of the band "II" was comparable to the intensity of band "I." For membranes modified with 1 : 1 solution, a slightly higher intensity of the carboxylic acid band was observed.

The literature survey has shown that the copolymers of NIPAM and AA were considered to be the random polymers.[10,11,15,19,20] Furthermore, for some copolymers, the lower contents of

carboxylic groups were noted than in the starting monomer mixture.[21] This observation was rationalized by the dissolution of polymer chains in water when large excess of AA was used for synthesis. Additionally, for surface grafting, one should recall polymerization mechanism in hydrophobic environment. Taking these two points, it cannot be assumed that grafted copolymer has the same partition of functional groups as the mixture of monomers. Hence, an independent method for the evaluation of surface hydrophilicity is needed.

Plasma-activated grafting usually causes significant reconstruction of surface chemistry and alteration of surface energy. To monitor these changes, surface energy was calculated by means of the contact angle measurements. Unfortunately, the porous membranes could cause intrusion of liquid into pores which could falsify the contact angle reading. Therefore, the measurements were conducted in the dynamic mode and the "static" contact angle was extrapolated to zero time. This approach is shown for water (Figure 3).

The change of surface energy as well as surface polarity is shown in Figures 4 and 5. It could be noted that both values increased when the mixture of monomers contained more AA. These relationships showed that hydrophilicity of surface, related to the presence of carboxylic groups, grew with the increase of AA contents. This is coherent with IR studies discussed earlier.

The morphology of PP membrane grafted with PAA, PNIPAM, and PAA-*co*-PNIPAM 1 : 1 is shown in Figure 6. The shape of water droplet was set in the left corner of the SEM image. A significant change of membrane structure could be observed after grafting the smart polymers.

The SEM images pointed that the pore diameter altered when the membrane was grafted by the stimuli-responsive polymers.
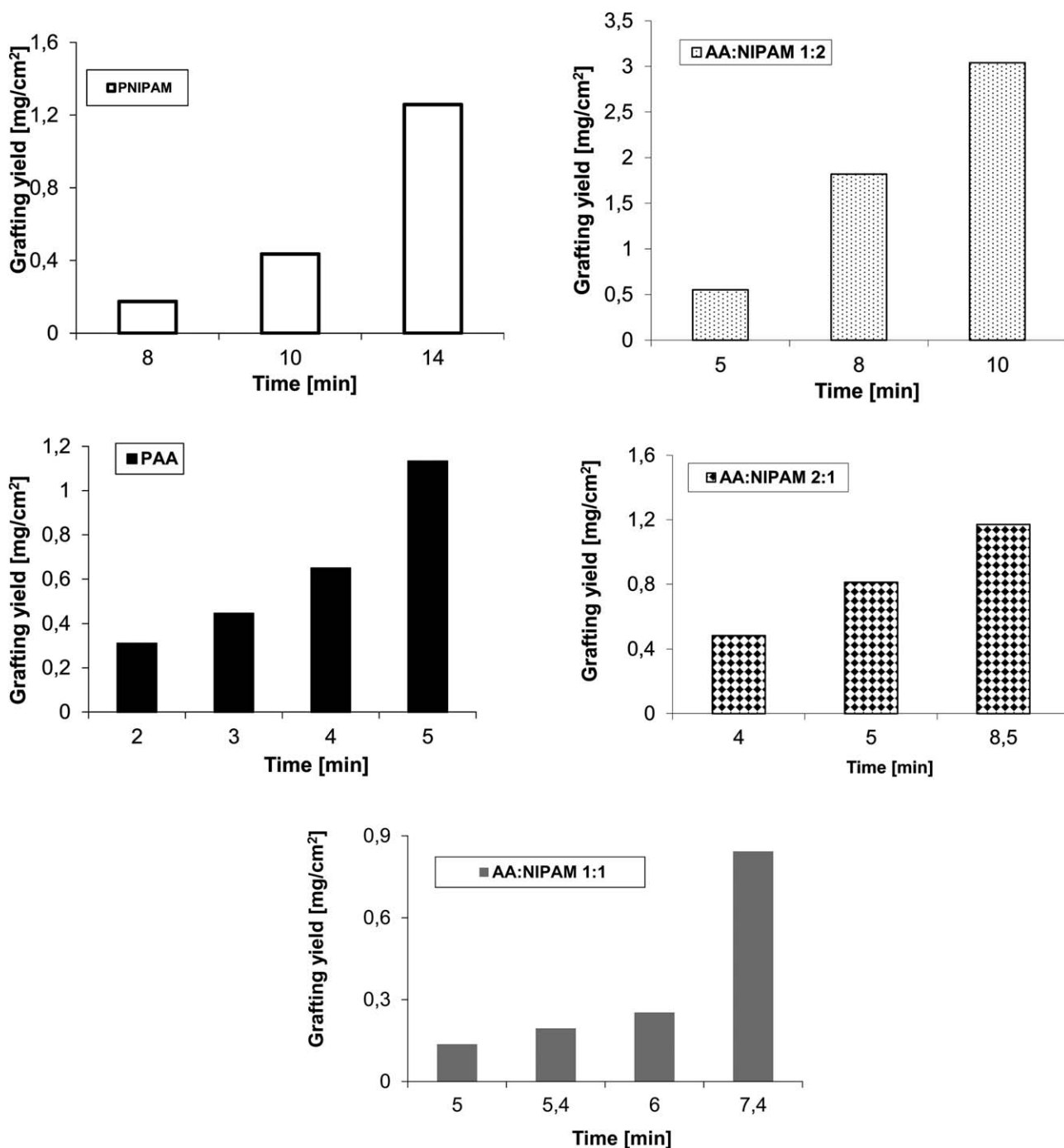
Figure 7. The grafting yield in relation to the irradiation time and to monomer mixture being used.

To better characterize the obtained materials, an average diameter of pores was calculated (Table II). As it was expected, the size of the pores was controlled by the external stimulus. The membranes with GY of about 0.1 mg/cm^2 were completely impermeable at 20°C and at a pH of 5.5. It indicated that their pores were blocked. At 20°C and pH 3.0, when the grafted chains collapsed, the pore size was comparable to a size of the nonmodified membranes. At 45°C and at pH 3.0, a slight decrease of pore size for membranes with the lowest grafting yield indicated the presence of some polymer chains on the pore walls. Significant reduction of pore size, independent of the pH and temperature, was observed for grafting yield of 1.0 mg/cm^2. We believed that it was the result of pore blockage by a high number of grafted chains.

Grafting yield was found to be a critical parameter for membrane preparation. Figure 7 shows the course of grafting yield with irradiation time. For all mixtures, a higher amount of polymer was grafted to membrane at longer time. However, grafting of AA or mixture containing more AA appeared faster than grafting of NIPAM. The outcome of this study is as
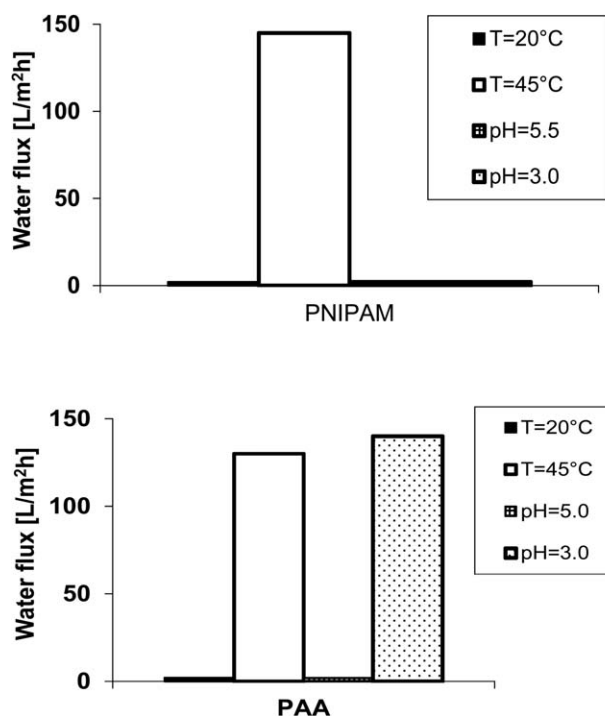
Figure 8. The effect of pH and temperature on the PP/PAA and PP/PNI-PAM membranes' permeability.

follows: to obtain membrane with the same amount of grafted polymer, the optimization process should be conducted for each system separately.

The evaluation of the membrane sensitivity to an external stimulus showed that the effect was observed for membranes grafted with a yield of <0.3 mg/cm^2. In the case of a higher grafting yield, pores were plugged with polymer and membrane did not show any volumetric flux.

The water flux through the nonmodified membranes, which was measured at a pressure of 0.05 MPa, was equal to 140 L/m^{2}h. It seems that the increase of membrane permeability at 45°C, in relation to permeability at 20°C, resulted from the change of water viscosity. At 20°C, the membranes grafted with PNIPAM were impermeable to water solutions of pH values of 3.0 and 5.5. This indicated the lack of PNIPAM's sensitivity to any pH changes. However, after rising temperature to 45°C, the PNIPAM-grafted membrane became permeable and the permeate flux increased to 145 L/m^{2}h. The membranes with PAA brushes were sensitive not only to pH value but also to temperature. At 20°C and at a pH of 5.5, the PAA-grafted membranes were impermeable. Although, at pH 3.0, when the measurements were carried out at 20°C, the volumetric flux increased to 140 L/m^{2}h. The permeability of membrane at 45°C and at pH of 5.5 reached 130 L/m^{2}h (Figure 8).

The use of membranes grafted with copolymer of PAA/PNIPAM altered the permeability of membranes also. It was observed that not only the amount of grafted copolymer, but also its composition, affected the flux value. Figure 9 shows the volumetric flux through membranes with respect to both the stimuli and the composition of grafted chains. All membranes were

permeable at 45°C and at pH of 3.0 and impermeable at 20°C and at pH of 5.5 when grafted chains were expended owing to hydrophobic interactions (NIPAN) or ionic and hydrophobic interactions (AA). The membrane permeability reached the value characteristic for PP/PAA (Figure 8) when membranes were grafted with 1 : 1 and 2 : 1 PAA/PNIPAM copolymers. It could suggest the contribution of hydrophobic interactions of AA segments to the "coil-to-globule" transition behavior. The effect of NIPAM on the transition of PAA was also noted. At pH 3.0, the volumetric flux was sensitive to the amounts of acrylamide and was equal to 135, 130, and 120 L/m^{2}h with the increase of the NIPAM content.

As the response of PNIPAM to temperature is very fast, after 1 min at 45°C, the membrane was completely permeable to water. The PAA, however, responded much slower to the temperature changes. It seems that complete reconstruction of the grafted
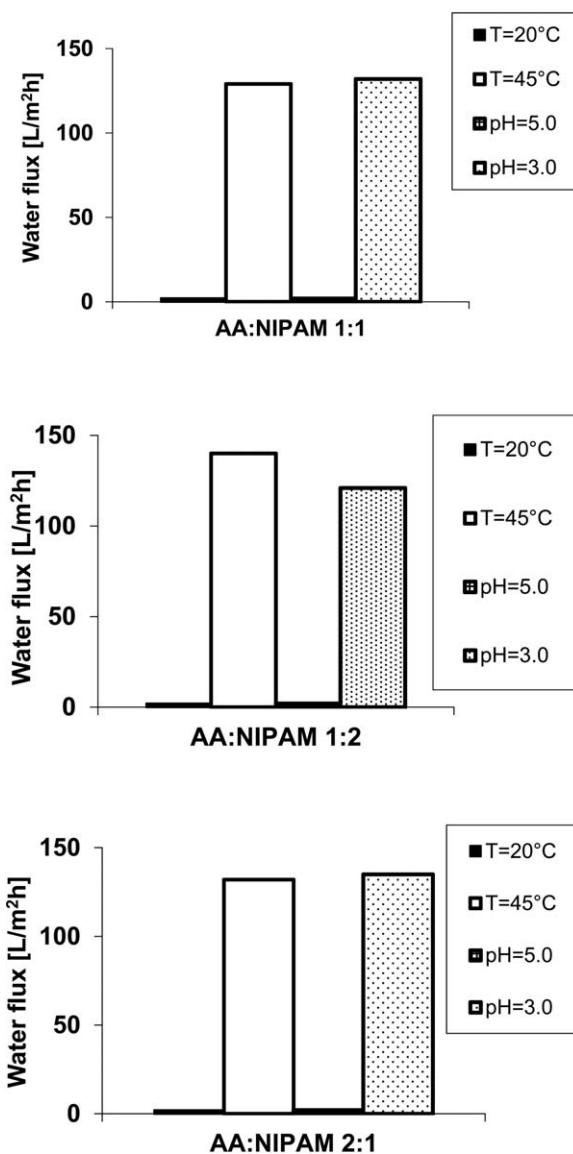
Figure 9. The effect of pH and temperature on the membrane permeability. The case of AA-NIPAN copolymers.
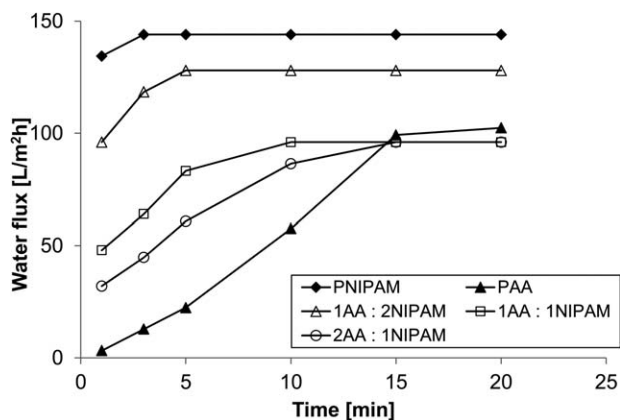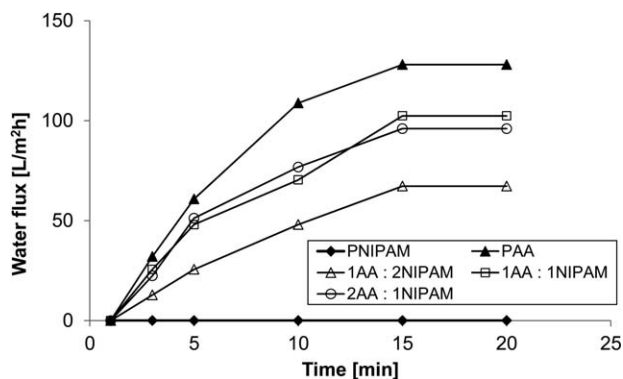
**Figure 10.** The effect of time on pure water flux at pH of 5.5 and temperature change from 20 to 45°C.

chains appeared within 15 min (Figure 10). In the case of the membranes with grafted copolymers PAA/PNIPAM, the rate of response grew with the increase of content of the PNIPAM in the polymeric chains.

It was noted that PNIPAM chains did not respond to the changes of pH (Figure 11), whereas the properties of membranes with grafted copolymers PAA/PNIPAM were altered with either pH or temperature. Furthermore, the rate of response to the changes of pH was similar for the membranes of PAA and PAA/PNIPAM.

The grafting chains of copolymers allowed obtaining membranes with pores whose size was dependent on the environment conditions. It meant that with the change of solution's pH or temperature, it is possible to control the membrane rejection properties. Figures 12 and 13 show the course of the permeate flow with respect to the solution pH value. Two kinds of membranes grafted with copolymer, AA : NIPAM 1 : 1 and 1 : 2, were compared to the membranes grafted with AA or NIPAM. The studies were conducted at 20 and at 45°C. For AA : NIPAM 1 : 1 membranes worked at 45°C, the average pore size varied from 0.05 μm at pH of 3.0 to 0.031 μm at pH of 6.5. The same membrane applied at 20°C changed the pore diameter from 0.030 μm at pH of 3.0 to 0 μm at pH of 6.5. In the case of AA : NIPAM 1 : 2 membranes, the pore diameter varied from 0.05 μm at pH of 3.0 to 0.028 μm at pH of 6.5 at 45°C, and from 0.040 μm at pH of 3.0 to 0.017 μm at pH of 6.5

Figure 11. The effect of time on pure water flux at 20°C and pH change from 3 to 5.5.
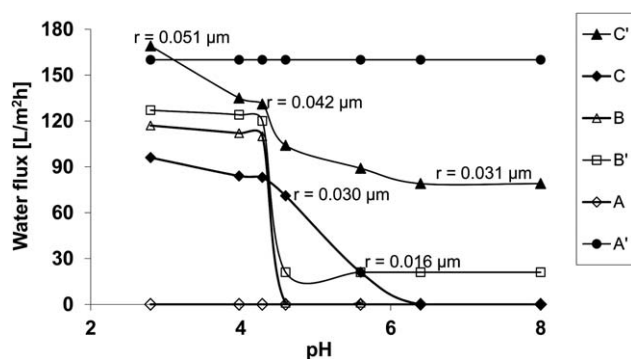
Figure 12. The effect of pH value on the permeate flux and the pore's size on solution's pH, for NIPAM (A-20°C, A′-45°C), AA (B-20°C, B′-45°C), AA : NIPAM 1 : 1 (C-20°C, C′-45°C) membranes.
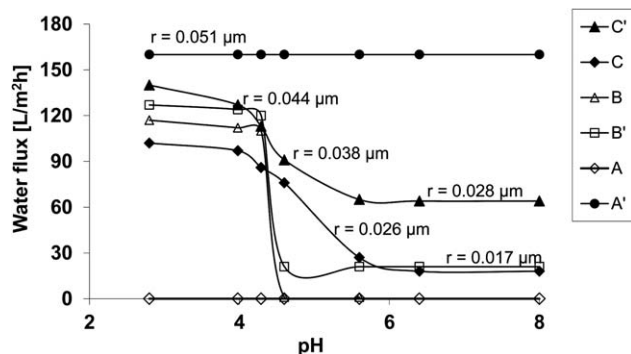
Figure 13. The effect of pH value on the permeate flux and the pore's size on solution's pH, for NIPAM (A-20°C, A′-45°C), AA (B-20°C, B′-45°C), AA : NIPAM 1 : 2 (C-20°C, C′-45°C) membranes.

when the membrane was tested at 20°C. The pore size of the NIPAM membranes did not change with the solution's pH. In the case of AA membranes, the pores were either opened or closed according to the pH of the solution. The AA : NIPAM membranes can be successfully used for the separation of various compounds and their separation properties will vary according to the changes of environmental conditions.

Another application of the described membranes is their use in a controlled separation of one compound. Table III lists the

Table III. The Dependence of Solute Retention (R) BP on Solution's pH and Temperature

| pH | Solution temperature (°C) | AA : NIPAM membranes | |
| | | 1 : 2 | 1 : 1 |
		R (%)	
6.50	20	80	100
	45	70	65
5.25	20	62	85
	45	58	45
3.00	20	36	59
	45	30	26

degree of retention for BP, in relation to the used membrane, pH solution, and temperature. For the AA : NIPAM 1 : 2 membranes, solute rejection varied from 30 to 90%. In the case of AA : NIPAM 1 : 1 membranes, the R-value varied from 26 to 100% depending on the external conditions.

CONCLUSIONS

The plasma modification of polypropylene membranes efficiently changes the nature of the membrane surface. As a result of the plasma-induced polymerization, the membranes could be grafted with the chains of smart polymers as PNIPAM or PAA. The obtained intelligent membranes showed sensitivity to temperature and to pH changes.

With the increase of exposition of plasma-activated samples to UV radiation, the grafting yield of membranes increased significantly. However, the grafting yield should not exceed the value of 0.3 mg/cm^2 when the membrane valves were the preparation targets. For larger yields of grafting, the membranes were impermeable to solution. Owing to the various rates of polymerization, each monomer system should be evaluated separately to control the extent of grafting and to select the optimal modification time.

The modified membranes can be used as stimuli-responsive membranes for various processes. The grafting of smart polymers makes it a more versatile separation tool that tunes the separation properties with respect to the external stimuli.

The grafting of NIPAM and AA copolymer allows to prepare bifunctional membranes that respond simultaneously to the alteration of solution temperature and pH. The properties of such membranes can be tailored by adjusting the ratio of both monomers used for grafting.

ACKNOWLEDGMENTS

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