

Synthesis and Properties of Water Soluble Polyurethanes Based on Poly(ethylene glycol)

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ABSTRACT: Water soluble polyurethanes (WSPU)s have been prepared by polycondensation of isophorondiisocyanate and tolylene-2,4-diisocyanate with poly(ethylene glycol)s (PEGs) of molecular weights 400, 600, and 1,000. The physicochemical properties of the WSPUs depend on the hydrophilic–hydrophobic balance in their polymeric chain, i.e., the properties are determined by relative density of the hydrophobic diisocyanate residues in WSPU. X-ray and differential scanning calorimetry studies show that the WSPUs have a degree of crystallinity lower than that of the pure

PEGs of the same molecular weights. Like the PEGs the WSPUs prepared form interpolymer complexes with polyacrylic (PAA) and polymethacrylic (PMAA) acids. These complexes are more stable than the (PEG.PAA) and (PEG.PMAA) complexes. The novel compounds can be considered as modified linear PEGs. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3651–3658, 2004

Key words: water soluble polyurethanes; hydrophilic–hydrophobic balance; polyacid–polyurethanes complexes

INTRODUCTION

Polyurethanes (PUs) based on poly(ethylene glycol) (PEG) and diisocyanate (DIC) can be considered either as modified (hydrophobized) PEG or as a PU comprising hydrophilic PEG chains. The physicochemical and physicomechanical properties of the water-swelling networks based on PEG and DIC depend on the hydrophobic–hydrophilic balance. Polyols could be used as a crosslinking agent. Studies of polymer networks prepared by polycondensation of aromatic DIC with PEGs having different molecular weights have been reported.^{1–3} Trimethylolpropane and hexanetriol have been used as crosslinking agents. The networks thus prepared belong to the class of hydrogels. The physicochemical properties and the swelling degree in water of such hydrogels depend on the PEGs molecular weights as well as on the concentration of triol. The higher PEG molecular weight is, the higher the swelling degree. On the other hand the latter decreases with increasing temperature and triol concentration.

Gnanou et al.⁴ have obtained hydrogels subjecting PEGs of different molecular weight to polycondensation with aromatic and aliphatic pluriisocyanates, i.e., with compounds comprising three and more isocya-

nate groups. These compounds are also able to act as crosslinking agents. The hydrogels prepared have good enough mechanical strength, high hydrophilicity, and optical transparency. Hence, they have potential for applications as medical materials.

Studies on the aqueous dispersions of PU ionomers are well known.^{5–9} Quaternized diols have been used to obtain cationomers to act as partners of DIC in the polycondensation reaction. Diols comprising salt bonds with cations as counterions have been used to prepare PU anionomers. Ion comprising PU dispersions are used in versatile technical fields, as coverings for fibers, paper, fire resistant impregnates, and leather dressings.

The studies of water soluble PU (WSPU) are limited to WSPU comprising PEGs as a main chain and hydrophobic alkyl end groups.^{10–13} These polymers in solution are able to form micelles. Increasing their concentration leads to the formation of a physical polymer network, i.e., to the formation of a hydrogel.

The aim of this work is the synthesis and investigation of the properties of WSPUs, comprising hydrophilic PEG chains of various molecular weights.

EXPERIMENTAL

Isophorone diisocyanate (IPDI) and tolylene 2,4-diisocyanate (TDI) (Fluka) were distilled under vacuum in argon atmosphere. The bp of IPDI is 152–153°C/10 mm Hg and that of TDI is 116–117°C/10 mm Hg.

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PEGs of molecular weights 400, 600, and 1,000 (Fluka) were dried under argon at 100°C/0.1 mm Hg for 2 h. The PEGs of molecular weights 1,500, 2,000, 3,000, 6,000, 15,000 and 40,000 (Fluka) were used without further purification.

The polycondensation of DIC with PEG was run at constant stirring under argon at 100–110°C for 6 h. To obtain PUs of various molecular weights the reaction mixtures were at different DIC : PEG molar ratios. The PUs prepared will be further on denoted as: 4P12 for samples of PEG molecular weight 400 prepared by polycondensation of IPDI with PEG at IPDI : PEG molar ratio 1 : 2; 4P23 for samples of PEG molecular weight 400 prepared by polycondensation of IPDI with PEG at IPDI : PEG molar ratio 2 : 3, etc. The abbreviations 6P12 and 10P12 correspond to samples of the same composition as 4P12 but the molecular weights of the PEGs used were 600 and 1000. The samples prepared via polycondensation of TDI and PEG have analogous abbreviations as those of IPDI-PEG system, with the sole difference that instead of "P," "T" is used, e.g., the abbreviation 10T23 means that the sample was prepared via polycondensation of TDI with PEG of molecular weight 1000 at TDI : PEG molar ratio 2 : 3.

The molecular weights of PUs were determined by GPC analyses using Ultrastayragel columns with pore sizes 100, 100, 500, and 1,000 Å, eluent THF. The detection was UV in cases of the T samples and refractometric in the cases of the P samples. PEGs of various molecular weights were used as standards.

The quantity of HO- end groups in the PUs obtained was determined according to the well-known acetylation method described by Kasterina and Kalina.¹⁴ Particularly this was the method used to determine the content of HO- groups in phenol-formaldehyde resins.¹⁵

The IR spectra were taken on a Bruker Vector 22 spectrometer in KBr pellets.

A Perkin-Elmer DSC-7 was used for determining the melting temperatures T_m and the heats of fusion ΔH_{fus} of the PUs obtained and of the PEGs. All measurements were calibrated with indium and plumbum. The scans were carried out at a heating rate of 10°C/min in argon atmosphere.

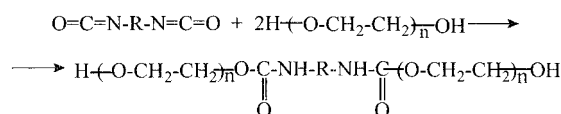
The X-ray diffraction patterns of the samples were obtained on an X-ray diffractometer Philips Θ -2 Θ Bragg-Brentano geometry using $\text{Cu}_{K\alpha}$ radiation ($\lambda = 1.54178\text{\AA}$) and mounted graphite monochromator for the diffracted beam. The diffraction data were collected for 10 s at each 0.02° step width over a 2 Θ range from 5 to 60°.

The potentiometric studies were carried out on a Radelkis OP 208/I (Hungary) pH meter equipped with combined glass electrode OP 0808 P.

Viscometric data were obtained at 25°C using an Ubbelohde viscometer.

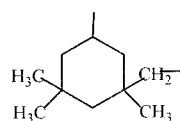
RESULTS AND DISCUSSION

PUs based on PEG have been prepared according to the above-mentioned procedure. In the case of a DIC : PEG molar ratio 1 : 2, the reaction proceeds according to:



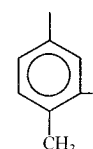
where

R=



isophorone residue

or R=



2,4-tolylene residue

$n = 9, 14,$ and $23,$ respectively, molecular weight of PEG = 400, 600, and 1,000.

In the general case at DIC : PEG molar ratio $m : (m + 1),$ the PU prepared will comprise m DIC residues and $(m + 1)$ PEG chains. Hence, any PU macromolecule will have PEG chains as end fragments.

Table I presents the molecular weights of the PUs, the aggregation state, and the water solubility of the samples at 25°C. As a quality criterion of the water solubility of PUs, the mixture PU + H₂O at 1% mass concentration of PU has been used. As seen, the PUs based on PEGs of molecular weight 600 and 1,000 at 25°C are in the solid state. The relatively low density of the urethane groups (UGs) in this case does not hamper the formation of the partially crystal PEG phase.

The situation in the case of PUs based on PEGs of molecular weight 400 is a different one. The samples comprise more UGs whose presence hampers the formation of a PEG crystalline phase and, respectively, the stiffening of the samples. These samples are highly viscous liquids.

The water solubility of PUs depends also on the concentration of UGs in the polymeric chains. PUs based on PEGs of molecular weight 600 and 1,000 are water soluble. In the case of PUs based on PEG of molecular weight 400, only the samples of not very high molecular weight are soluble in water. The higher density of the UGs leads to hydrophobization of the PU macromolecules. Therefore the polymer becomes insoluble.

As seen from Table I, the real molecular weights of the PUs prepared are higher than the calculated M_{cal} according to the reaction in Scheme 1 for the different

TABLE I
Molecular Weight Characteristics of the PUs Based on PEG Determined by GPC, the Theoretically Calculated Molecular Weight, Aggregation State, and Solubility in Water at 25°C

| Sample | \bar{M}_w | \bar{M}_n | \bar{M}_w/\bar{M}_n | M_{cal} | Aggregation State | Solubility in Water |
|--------|-------------|-------------|-----------------------|-----------|-------------------|---------------------|
| 4P12 | 3,300 | 2,250 | 1.47 | 1,022 | Liquid | Soluble |
| 4P23 | 5,300 | 3,000 | 1.77 | 1,644 | Liquid | Insoluble |
| 4P34 | 6,400 | 3,300 | 1.94 | 2,266 | Liquid | Insoluble |
| 4P910 | 11,300 | 4,200 | 2.69 | 5,998 | Solid | Insoluble |
| 4T12 | 2,200 | 1,400 | 1.57 | 974 | Liquid | Soluble |
| 4T23 | 3,900 | 1,800 | 2.17 | 1,548 | Liquid | Insoluble |
| 4T45 | 6,600 | 2,600 | 2.54 | 2,696 | Solid | Insoluble |
| 4T910 | 9,800 | 3,100 | 3.16 | 5,566 | Solid | Insoluble |
| 6P12 | 4,600 | 2,100 | 2.19 | 1,422 | Solid | Soluble |
| 6P23 | 6,800 | 3,000 | 2.27 | 2,242 | Solid | Soluble |
| 6P910 | 17,400 | 5,100 | 3.41 | 7,982 | Solid | Soluble |
| 10P12 | 5,100 | 2,800 | 1.82 | 2,222 | Solid | Soluble |
| 10P23 | 7,900 | 3,500 | 2.28 | 3,444 | Solid | Soluble |
| 10P45 | 11,300 | 4,680 | 2.14 | 5,888 | Solid | Soluble |
| 10P910 | 15,900 | 6,200 | 2.56 | 11,998 | Solid | Soluble |
| 10T12 | 4,400 | 2,400 | 1.83 | 2,174 | Solid | Soluble |
| 10T23 | 7,200 | 3,400 | 2.12 | 3,348 | Solid | Soluble |
| 10T56 | 10,100 | 4,100 | 2.46 | 6,870 | Solid | Soluble |

DIC : PEG molar ratios. This can be explained by the following two reasons

First, the molecular weights of PUs determined by GPC are higher than M_{cal} because of the formation of associates in THF solution. The UGs are capable of forming hydrogen bonds between each other and with oxygen atoms of the ethers and in particular with the oxygen atom of PEG^{16,17} as well. The availability of PUs intermolecular associates in a THF solution is proved by GPC chromatograms presented in Figures 1 and 2. The eluent volume $V_e = 21.4$ mL is the one where the first high molecular weight fractions 4P45 and 4T45 appear. This corresponds to $M \approx 4 \times 10^4$. Such a high M value proves the availability of intermacromolecular PU associates in the THF solution. As seen from Figure 1, for 4P12 and 4T12 the fraction of the highest macromolecular weight occurs at $V_e = 23.2$ mL. It is higher than V_e for 4P45 and 4T45 and corresponds to $M \approx 1.1 \times 10^4$. The molecular weights of the associates of 4P45 and 4T45 are greater than those of 4P12 and 4T12. It can be explained by the fact that the

higher molecular PU chains are more likely to form intermolecular hydrogen bonds. It should be noted that M of the associates is not affected by the chemical nature of DIC: $V_e 4P12 = V_e 4T12$ and $V_e 10P45 = V_e 10T45$.

The GPC chromatograms on Figures 1 and 2 are qualitatively analogous. The difference is in V_e , at which the fraction of the highest molecular weight occurs. In the case of PUs based on PEGs of molecular weight 1,000, V_e is lower than that of PUs based on PEG-400. For 10P45 and 10T45, $V_e = 20.8$ mL, corresponding to $M \approx 6.4 \times 10^4$ and, for 10P12, and 10T12 $V_e = 22.3$ mL, corresponding to $M \approx 2 \times 10^4$.

The greater molecular weight of the associates in the 10P and 10T series compared to that in 4P and 4T series is due to the higher molecular weight of PUs based on PEG-1000 synthesized at the same ratio DIC : PEG = $m : (m + 1)$ of the reaction mixture.

Another reason for the disagreement in the molecular weights of PUs determined by GPC and M_{cal} is

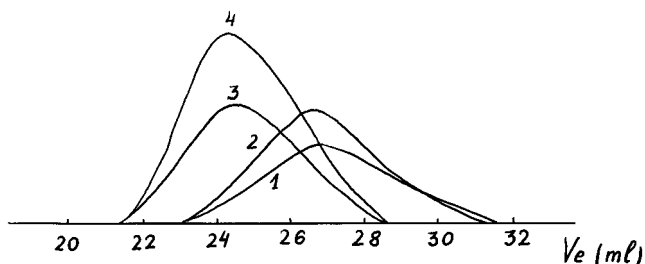


Figure 1 GPC chromatograms of (1) 4P12; (2) 4T12; (3) 4P45; and (4) 4T45. Eluent was THF.

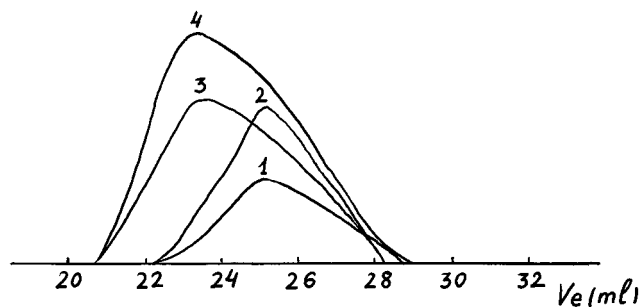


Figure 2 GPC chromatograms of (1) 10P12; (2) 10T12; (3) 10P45; and (4) 10T45. Eluent was THF.

TABLE II
Hydroxyl End Groups Contents (%) in Some of the
Water-Soluble Polyurethanes

| Sample | Calculated | Found experimentally |
|---------|------------|----------------------|
| PEG 400 | 8.50 | 8.47 |
| 4T12 | 3.49 | 3.54 |
| 4T23 | 2.19 | 2.32 |
| 4T45 | 1.26 | 1.19 |
| 4P12 | 3.33 | 3.21 |
| 4P23 | 2.07 | 1.96 |
| 4P34 | 1.15 | 1.21 |

the fact that high molecular weight PU fractions are probable to occur in the polycondensation mixture at any DIC : PEG = $m : (m + 1)$ since the free HO- end groups of PEG in the PU macromolecule are able to react with DIC molecules and extend the material polymeric chain. Therefore, the molar ratio DIC residues: PEG in the high molecular weight PU fraction should be different from the DIC : PEG = $m : (m + 1)$ ratio in the initial polycondensation mixture. That means the final product should comprise free unreacted PEG macromolecules. The existence of free PEG macromolecules should be detected by the GPC chromatograms of the polycondensation products, i.e., the molecular weight distribution should be bimodal. As seen from Figures 1 and 2, GPC chromatograms have a monomodal pattern. This is evidence of the lack of significant amounts of unreacted PEG in final product of reaction (I). Hence, the real molecular weights of PUs should be close to M_{cal} .

The method for determining the quantity of HO- groups in PUs macromolecules has been used to estimate the real average molecular weights of the prepared PUs.

The experimental data, presented in Table II, concern PUs based on PEG having $M = 400$, as with the increase in the molecular weight of PEG to 600 and 1,000, the concentration of HO- groups in the mixture analyzed lowers and the error in the determination of their amount becomes greater. It is worth mentioning that samples 4T23, 4T45, 4P23, and 4P34 are insoluble in water. They are soluble in the solution under analysis using the acetylation method. The theoretical HO- percentage content in the PUs samples is calculated assuming that the real average molecular weight of PU is the same as M_{cal} . The data for the initial PEG of $M = 400$ are given as a criterion of the reliability of the method used. As seen from Table II, the experimental data on the calculation of HO- percentage content in the PUs samples are in satisfying agreement with the theoretical calculations based on M_{cal} .

This allows us to conclude that the polycondensation reaction (I) yields PU, whose molar composition is practically identical with the MIC : PEG = $m : (m + 1)$

composition of the polycondensation mixture. That means the molecular weights determined by GPC are higher than M_{cal} because of the intermolecular associates occurring between the PU macromolecules in THF.

The PUs synthesized according to reaction (I) have urethane bonds in their polymer chain. Figure 3 plots the IR spectra of the initial DIC and PEG as well as those of PUs prepared at a ratio DIC : PEG = 3 : 4.

The spectra of DIC shown in Figures 3(a) and (b) have an intensive band at $2,261 \text{ cm}^{-1}$ for IPDI and at $2,266 \text{ cm}^{-1}$ for TDI. This is a typical absorption band for the valency vibrations $\nu_{N=C=O}$ of the isocyanate group.¹⁸ The IR spectrum of IPDI [Fig. 3(a)] has an absorption band at $2,956 \text{ cm}^{-1}$ assigned to the valency vibrations ν_{CH} in the isophorone residue.

There are two absorption bands in the IR spectrum of PEG shown in Figure 3(c), $\nu_{OH} = 3,475 \text{ cm}^{-1}$ and $\nu_{CH} = 2,870 \text{ cm}^{-1}$, corresponding to the valency vibrations in the hydroxyl end groups and to the C-H bonds in the PEG chains.¹⁹

There is no absorption band $\nu_{N=C=O}$ at $2,260 \text{ cm}^{-1}$ in the IR spectra of PUs [Figs. 3 (d) and (e)], which means that all isocyanate groups in DIC have reacted with the macromolecules of PEG. Accordingly, an absorption band for the valency vibrations $\nu_{C=O}$ in the UG appears at $1,717 \text{ cm}^{-1}$ in the spectrum of the PEG-IPDI system and at $1,728 \text{ cm}^{-1}$ in the PEG-TDI system.¹⁸ The band at about $3,320 \text{ cm}^{-1}$ is assigned to the valency vibrations ν_{NH} in the UG.²⁰ The UG gives also a band for the valency vibrations ν_{C-N} at $1,538 \text{ cm}^{-1}$. The remaining absorption band at $2,870 \text{ cm}^{-1}$ is for the ν_{C-H} vibrations in PEG chains. Thus the IR spectral data confirm that the formation of PU proceeds according to reaction (I).

Figure 4 presents the X-ray diffraction patterns of some PU samples based on PEG-1000. The X-ray diffraction patterns of the initial PEGs of molecular weights 1,000, 3,000, and 6,000 are also included for comparison. The X-ray diffraction patterns are normalized. Their evaluation allows the conclusion that the crystallinity degree of PU is significantly lower than that of the initial PEG of comparable molecular weight. This is explained in the change in the adequate chain crystallization of PEG caused by "foreign" UGs.

The crystallization degree of PUs has been determined by DSC. Figure 5 presents the thermograms of samples 10P23, 10T23, 10T56, and 10P910. The thermograms of PEGs of molecular weights 1,000, 3,000, 6,000, and 15,000 are presented as a comparison. First, it is seen that the melting points of PEGs are considerably higher than those of PU samples having comparable molecular weights. Second, DSC data allow the evaluation of the crystallinity degree X_c of each sample. X_c is calculated from the equation:

$$X_c = \frac{\Delta H_{fus}}{\Delta H_{fus}^0}$$

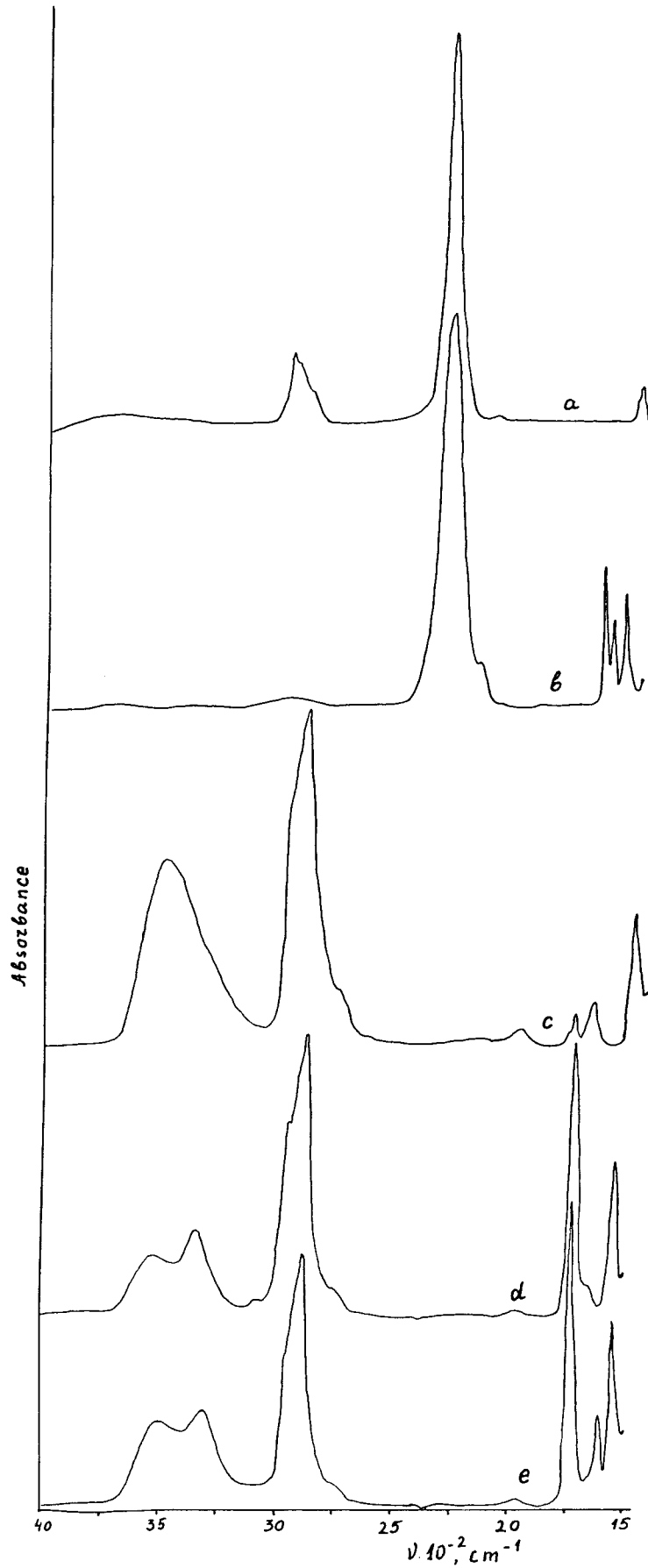


Figure 3 IR spectra of IPDI (a); TDI (b); PEG (c); 6P34 (d); and 6T34(e).

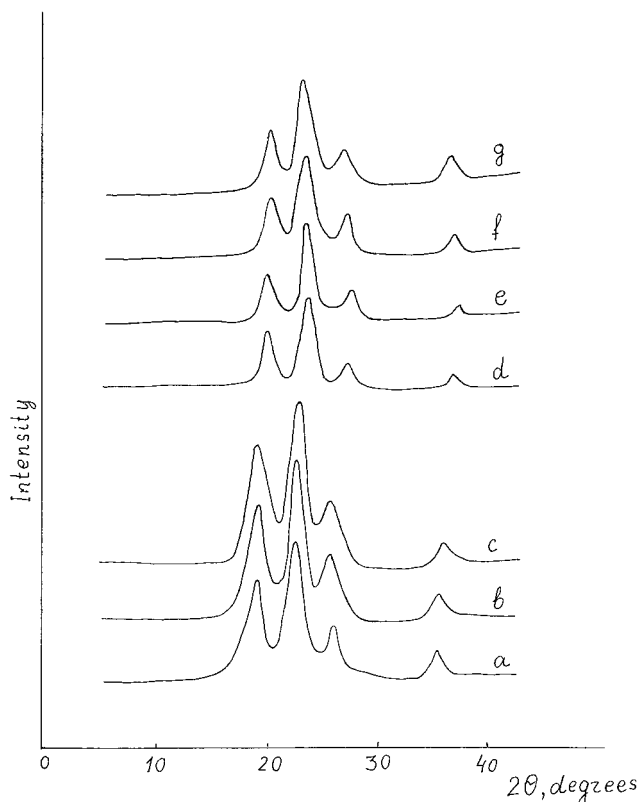


Figure 4 X-ray diffraction patterns of PEG: molecular weights 1,000 (a); 3,000 (b), and 6,000 (c) and of 10T23 (d); 10P23 (e); 10T56 (f) and 10P910 (g).

where ΔH_{fus}^0 is the heat of fusion of a perfectly crystalline polymer and ΔH_{fus} is the heat of fusion of the sample investigated determined from the thermo-

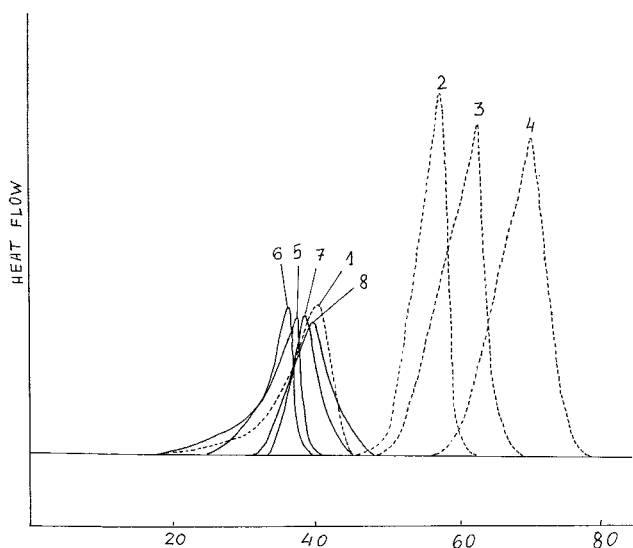


Figure 5 DSC thermograms for PEGs (dotted curves) and PUs (full curves). Molecular weights of PEGs: (1) 1,000; (2) 3,000; (3) 6,000; and (4) 15,000; (5) 10P23; (6) 10T23; (7) 10T56; and (8) 10P910.

TABLE III
Melting Temperature t_m , ΔH_{fus} , and X_c for Several Samples of PEGs and PUs

| Sample | t_m (°C) | ΔH_{fus} (J/g) | X_c (%) |
|-----------|------------|-------------------------------|-----------|
| PEG 1000 | 40 | 147 | 70.0 |
| PEG 3000 | 57 | 181 | 86.2 |
| PEG 6000 | 61 | 187 | 89.0 |
| PEG 15000 | 68 | 196 | 93.3 |
| 10P23 | 33 | 92 | 43.8 |
| 10T23 | 35 | 97 | 46.2 |
| 10T56 | 39 | 98 | 46.7 |
| 10P910 | 41 | 95 | 45.2 |

grams in J/g. According to the work of Li and Hsu²¹ and Jeon and Ree,²² the ΔH_{fus}^0 value of a 100% crystalline PEG is 210 J/g.

Table III presents the quantitative results from the DSC studies calculated from the plots on Figure 5. As seen, the melting temperatures t_m and the crystallinity degree X_c values for PEG and PU samples differ considerably. X_c values of all PEG samples are higher than those for PUs, regardless of the higher molecular weights of the PUs. The reason is the same: the "foreign" UGs hamper the formation of a PEG crystalline phase, due both to the steric hindrance and to the hydrogen bonds that the UGs form with the oxygen atoms of the PEG chains. Hence, the crystalline structure of PEG is destabilized.

It is known that PAA and PMAA form complexes with PEG in aqueous solution.^{23,24} The complex occurs as a result from the hydrogen bonds between hydrogen atoms from the undissociated carboxyl groups of the polyacids (PA) and the oxygen atoms in the PEG. The complexes (PA.PEG) in aqueous solution are stabilized by the hydrophobic interactions. That is why the WSPUs prepared should also form complexes with PAA and PMAA. The complex formation between PA and PEG is accompanied by a sharp decrease of the specific viscosity η_{sp} of the solution of the mixture PA + PEG. This decrease is caused by the formation of compact hydrophobic particles. The pH of the solution increases as a result of the bonding of the hydrogen atoms from the PA carboxyl groups to the oxygen atoms of PEG. The complex formation advances with the increase in the molecular weight of PEG. The dependence of the complex formation on the PEG chain length is described in detail.²⁵

Figure 6 presents the dependence of η_{sp} of the aqueous solutions of PAA + PUs mixtures on the weight ratio PU : PAA = φ . For comparison, η_{sp} of aqueous solutions of PAA + PEG mixtures with PEGs of molecular weights 6,000, 15,000, and 40,000 are presented. As seen from Figure 6 the formation of the (PAA.PEG) complex advances with the increase in the molecular weight of PEG. Noteworthy is the fact that the decrease of η_{sp} of the solution of the mixture PAA +

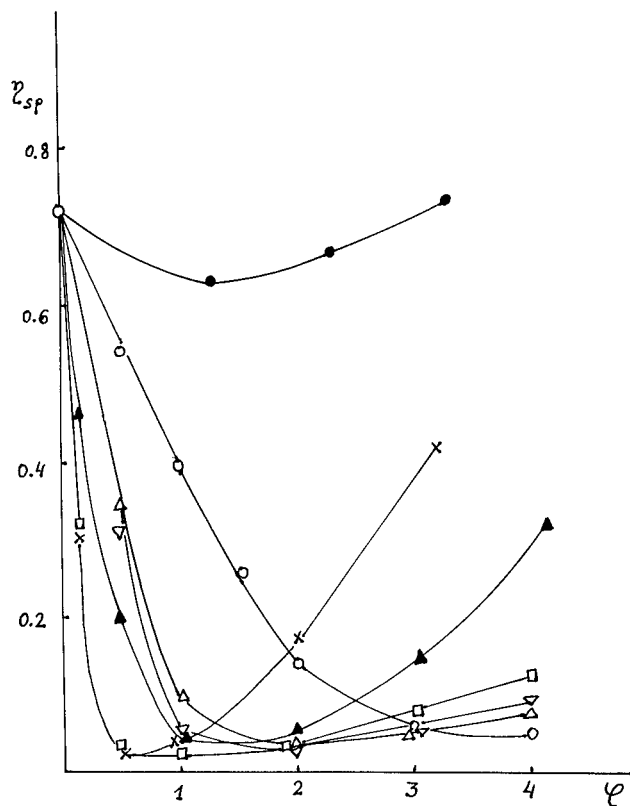


Figure 6 Plots of η_{sp} versus weight ratio ϕ for aqueous solutions of PAA with (○) 4P12; (△) 6P12; (▽) 10P12; (□) 10P45 and PEGs of molecular weights (●) 6,000; (▲) 15,000; (×) 40,000; $C_{PAA} = 0.1$ g/dL; 25°C.

4P12 is much greater than that of the solution of the PAA + PEG-6000 mixture. This means that the stability of the (PAA.4P12) complex is greater than that of the (PAA.PEG-6000) complex regardless of the lower

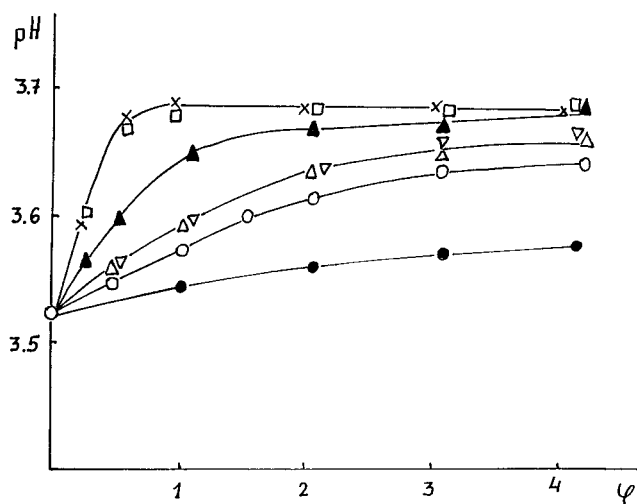


Figure 7 Plots of pH versus the weight ratio ϕ for aqueous solutions of PAA with PUs and PEGs. (○) 4P12; (△) 6P12; (▽) 10P12; (□) 10P45 and PEGs of molecular weights (●) 6,000; (▲) 15,000; (×) 40,000; $C_{PAA} = 0.1$ g/dL; 25°C.

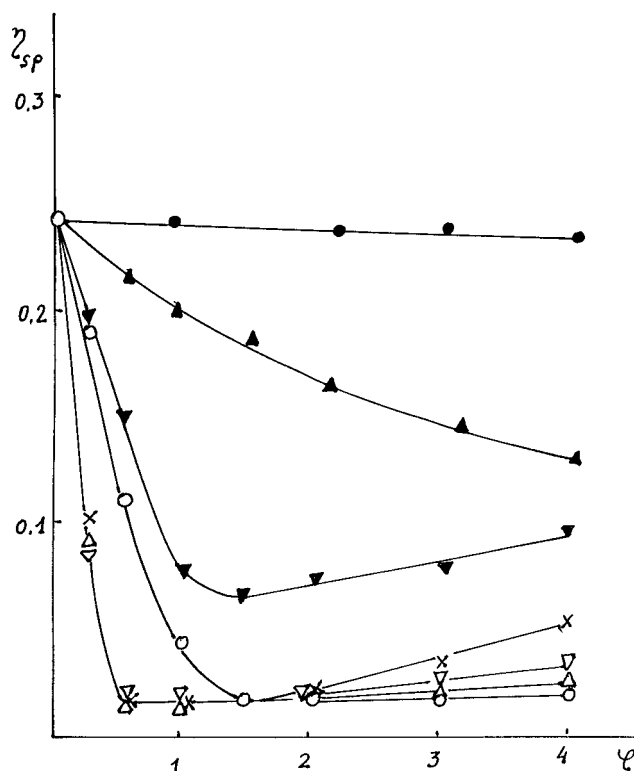


Figure 8 Plots of η_{sp} versus weight ratio ϕ for aqueous solutions of PMAA with (○) 4P12; (△) 6P12; (▽) 10P12 and PEGs of molecular weights (●) 1,000; (▲) 1,500; (▼) 2,000; (×) 3,000; $C_{PAA} = 0.1$ g/dL; 25°C.

molecular weight of 4P12. The greater stability of the (PAA.4P12) complex is explained by the additional stabilizing effect of the hydrophobic isophorone residue in the PU chain. A similar effect has been observed previously and studied in detail with regard to the formation of a complex between PAA and PMAA with monosubstituted PEG comprising hydrophobic groups of various chemical natures.^{26,27} The stability of the complex (PAA.10P45) is comparable to that of the (PAA.PEG40000) despite the fact that the molecular weight of 10P45 is significantly lower than that of PEG-40000.

The pH metric data are presented in Figure 7 and are in agreement with the data presented in Figure 6. The higher increase in pH of the solution of the PAA + PUs and the PAA + PEG mixtures, the more stable the complex is.

Figure 8 shows the dependence of η_{sp} of the aqueous solution of the mixture PMAA + PUs on ϕ . The same dependences for η_{sp} of PEGs having molecular weights 1,000, 1,500, 2,000, and 3,000 are presented for comparison. The complex (PMAA.PEG) is more stable than the one between PAA and PEG, keeping in mind the same molecular weight of PEG.^{24,25} The formation of the (PMAA.PEG) complex is observed even with PEGs of molecular weights 1,500–2,000. However, in this system the present isophorone residue also causes

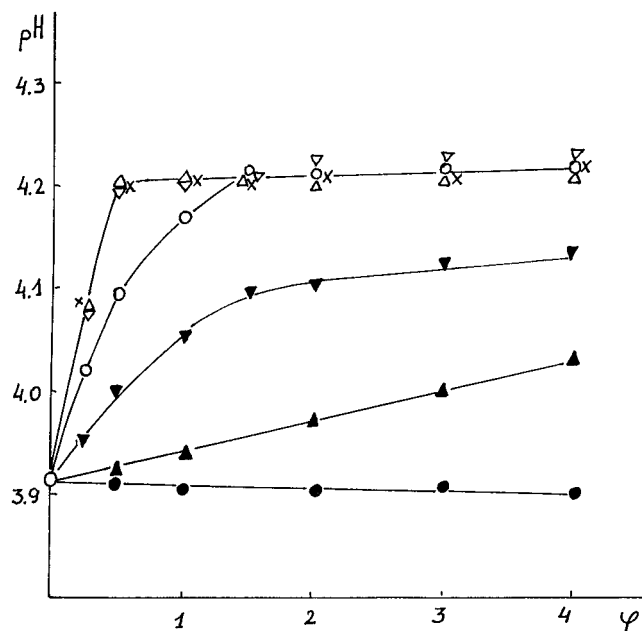


Figure 9 Plots of pH versus the weight ratio ϕ for aqueous solutions of PMAA with PUs and PEGs. (○) 4P12; (△) 6P12; (▽) 10P12 and PEGs of molecular weights (●) 1,000; (▲) 1,500; (▼) 2,000; (×) 3,000; $C_{PAA} = 0.1$ g/dL; 25°C.

stabilization of the complex, although this effect is less significant than that in the case of (PAA.PUs) complexes. The pH metric data given in Figure 9 are in agreement with those in Figure 8.

The complex formation of PA with PUs based on 4T and 10T occurs according to the same dependences as those of PUs based on 4P and 10P. Therefore we find it unnecessary to provide additional illustrative material in this paper.

CONCLUSION

The WSPUs obtained in this work can be considered as modified PEGs, comprising hydrophobic fragments from DIC. Changing the density of these fragments in PU chains one can regulate the hydrophilic–hydrophobic balance in the modified PEGs, thus influencing their physicochemical properties. This paper is a new contribution to the two currently known methods^{28–34} for chemical modification of PEG: γ - and UV-irradiation.

It is known that PUs can be modified via reacting them with NaH. The reaction yields a polyanion. This polyanion then can participate in various chemical reactions.^{35,36} Thus the PUs reported can be further modified using the UGs to introduce functional groups of various chemical nature into the PU polymer chain. The WSPUs functionalized via such methods can find application as polymeric carriers of physiologically active substances and drugs in particular.

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