COMPARATIVE EVALUATION OF SOME PROPERTIES OF TWO POLY(ETHER-IMIDE) THIN FILMS WITH/WITHOUT FLUORINE IN THE STRUCTURE

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Thin films, in the range of tens of micrometers thickness, have been prepared by casting onto glass plates the N-methylpyrrolidone solutions of two poly(ether imide)s containing isopropylidene or hexafluoroisopropylidene groups. The polymers have been synthesized by solution polycondensation reaction of 4,4′-(1,3-phenylenedioxy) diani-line with 2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride or 1,1,1,3,3,3-hexafluoro-2,2-bis[(3,4-dicarboxy-phenoxy) phenyl]propane dianhydride. They were easily soluble in polar aprotic solvents and showed high thermal sta-bility. The surface properties of the poly(ether imide) thin films such as dynamic contact angles and contact angle hys-teresis, static contact angles and water vapors sorption capacity were evaluated in correlation with their structure. Also, the free surface energy was determined by considering the static contact angle values.

INTRODUCTION

Among heterocyclic thermostable polymers, aromatic polyimides represent the most important class of heat resistant polymeric materials. They are well known to retain their excellent properties at high temperatures for long period of time. Some of these polymers have been widely used as high performance materials in the aerospace and elec-tronic industries due to their excellent thermal sta-bility, outstanding mechanical integrity, dimen-sional stability, good electrical properties and chemical resistance. However, polyimides are of-ten insoluble and intractable in their fully imidized form, presenting serious processing difficulties.[1,2] Various efforts have been made on the synthesis of soluble and processable polyimides without much sacrifice of their excellent thermostability. For this purpose chemical modifications of polyimides have been done, such as the introduction of flexi-ble linkages in their backbone or incorporation of bulky side groups.[3,4] The aromatic ether linkages

inserted into the aromatic main chains of the poly-imides lead to lower glass transition temperature as well as significant improvement in solubility and other characteristics of the polymers without greatly sacrificing other advantageous polymer properties. Thus the poly(ether imide)s exhibit, in the same time, high thermal stability and good solubility in organic solvents.[5-10]

The incorporation of hexafluoroisopropylidene (6F) groups into polymer backbones enhances the polymer solubility without decreasing thermal sta-bility. The retention of high thermal stability is attributed to the strong C–F bonds. Other effects of the 6F groups are the increased glass transition temperature and flame resistance with a concomi-tant decreased crystallinity, dielectric constant and water absorption.[11-15]

Here is presented the synthesis and characteri-zation of two poly(ether imide)s containing isopro-pylidene or 6F groups in the dianhydride segments. The polymers were prepared by solution polycon-densation of an aromatic diamine, namely 4,4′-

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(1,3-phenylenedioxy)dianiline, with two bis(ether anhydride)s which contain isopropylidene or 6F units. Some characteristics of thin films made from these polymers have been evaluated with respect to their chemical structure.

RESULTS AND DISCUSSION

Poly(ether imide)s **4** were prepared by thermal treatment of poly(amic acid)s **3**, which were obtained from 4,4′-(1,3-phenylenedioxy)dianiline, **2**, and 2,2-bis[(3,4-dicarboxyphenoxy) phenyl]propane dianhydride, **1a**, or 1,1,1,3,3,3-hexafluoro-2,2-bis[(3,4-dicarboxyphenoxy) phenyl] propane dianhydride, **1b**, (Scheme 1). The dianhydride **1b** was prepared according to a method previously published.[16]

The conversion of poly(amic acid)s **3** to the fully cyclized poly(ether-imide)s **4** was confirmed by IR and ^{1}H NMR spectroscopy. The complete conversion of *o*-carboxy-amide groups to the imide rings was confirmed by the disappearance of the absorption bands at 1660-1670 cm^{-1} and 2500-3000 cm^{-1}. In IR spectra of polymers **4** strong bands appearing at 1780-1770 cm^{-1} and 1720-1710 cm^{-1} were attributed to symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide rings. Absorption band at 1380 cm^{-1} was due to C−N stretching of imide rings, and absorption band at 740 cm^{-1} was due to imide ring deformation. Characteristic bands at 3060 cm^{-1} and 1600 cm^{-1} were due to aromatic C-H stretching and aromatic C=C stretching, respectively. The absorption band for ether linkages appeared at 1240 cm^{-1}. IR spectrum of polymer **4a** showed absorption bands at 2970 cm^{-1} and 2860 cm^{-1} due to the presence of isopropylidene groups. In the IR spectrum of polymer **4b** characteristic absorption bands appeared at 1180 cm^{-1} and 1210 cm^{-1} due to 6F groups.

Figure 1 illustrates the ^{1}H NMR spectrum of polymer **4b** with the assignments of all the protons.

The protons H_b closed to electron-withdrawing imide ring appeared at the farthest downfield region of the spectrum. The protons H_h and H_k shifted to higher field due to the electron donating properties of aromatic ether linkages. The imidization of the poly(amic acid) **3** was also confirmed by the fact that ^{1}H NMR spectrum of polymer **4** showed no residual resonance in the region 9-11 ppm indicating the absence of amide NH protons.

4a: R = $\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{|}}$; 4b: R = $\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{|}}$
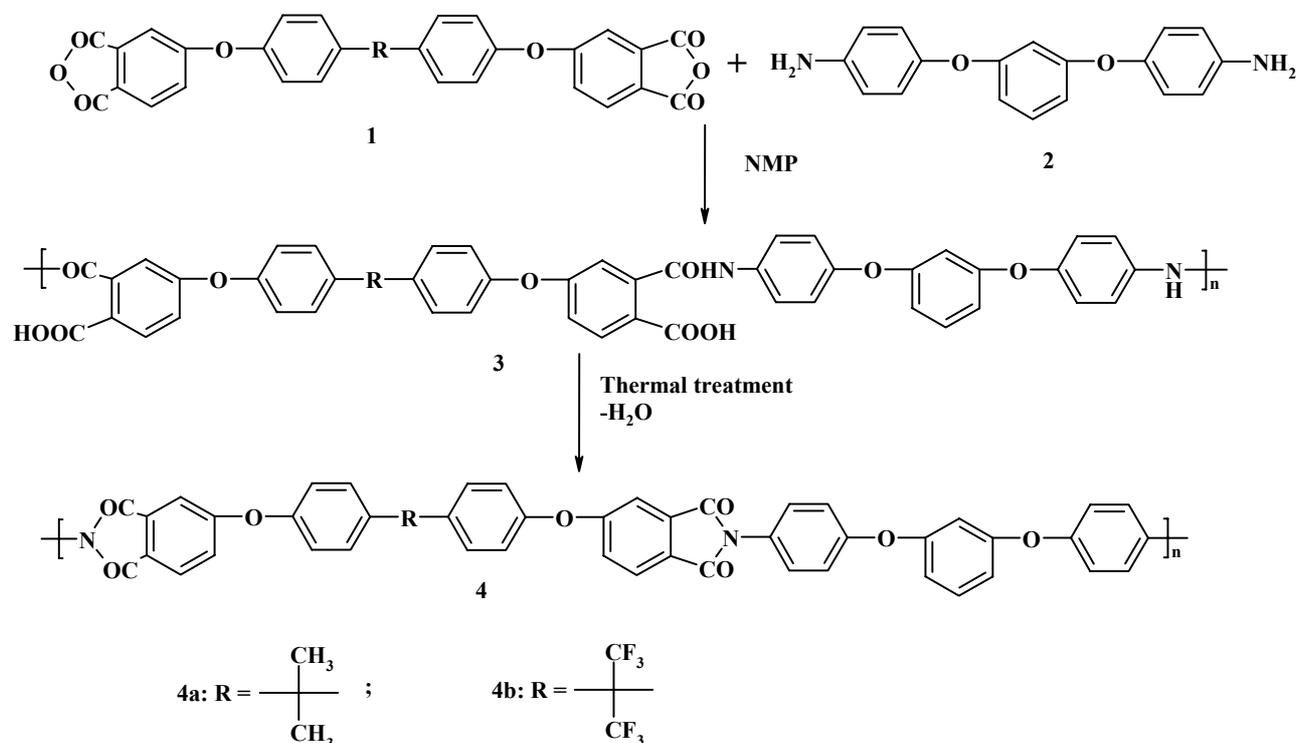
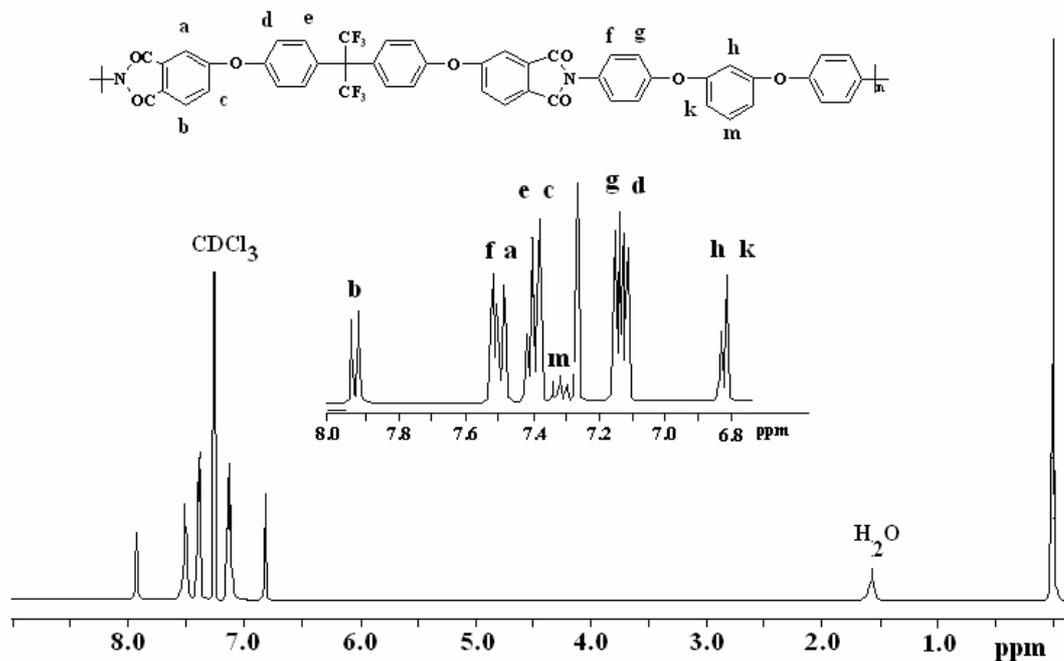Scheme 1 – Preparation of poly(ether imide)s **4**.

Fig. 1 – ^{1}H NMR of polymer **4b**.

The solution of poly(amic acid)s **3** in N-Methyl-2-pyrrolidone (NMP) having a concentration of about 10% were cast onto glass substrates and heated at different temperature up to 250°C to yield thin films of poly(ether imide)s **4** having a thickness of tens of micrometers. The polymers **4** exhibited good solubility in organic solvents such as NMP, N,N-dimethylformamide and chloroform. The inherent viscosity values of the polymers **4a** and **4b** were of 0.61dL/g and 0.54 dL/g, respectively, measured in NMP, at 20°C, at a concentration of 0.5 g/100 mL solvent.

The tensiometric method was used for measuring dynamic contact angles, by the Wilhelmy plate technique. Values obtained for advancing and receding contact angles with water for the two samples are presented in table 1. It can be seen that both contact angles increased by insertion of the fluorine atoms in the polyimide structure. This is naturally because, as it is known, the presence of fluorine atoms in the structure of the polymers increases their hydrophobic properties.[17]

It was calculated the difference between the maximum advancing and minimum receding contact angle values known as contact angle hysteresis - a measure of the surface heterogeneity and roughness.[18] The obtained values suggest that both samples had about the same heterogeneity on the film surface (~44 degrees).

The values of the liquid contact angles (water and ethylene glycol) determined by static method was 10 degrees lower as compared with those determined in dynamic regime.

The static contact angle values were used to calculate free surface energy also referred to as solid tension and described by their components, dispersive and polar, in the equations of Owens and Wendt.[19]

$$(1+\cos\theta)\gamma_L = 2(\gamma_s^d\ \gamma_L^d)^{1/2} + 2(\gamma_s^p\ \gamma_L^p)^{1/2}$$

Table 1

The main parameters of the water contact angle measurements

Polymer	Water dynamic angles			Static angles	
	θ_a^a	θ_r^b	H^c	Water	Ethylene glycol
4a	86.75	42.49	44.26	76.23	71.58
4b	89.50	44.77	44.73	80.55	68.47

^{a} Maximum advancing contact angle value, determined as average of the three measurements;
^{b} Maximum receding contact angle value; ^{c} H = $\theta_a - \theta_r$

The surface tension values for the two liquids and their components (mN/m) are for water: $\gamma_{L1}=72.8$, $\gamma_{L1}^{p}=51$, $\gamma_{L1}^{d}=21.8$, and for ethylene glycol $\gamma_{L2}=48$, $\gamma_{L2}^{p}=19$, $\gamma_{L2}^{d}=29$. By using the contact angles on the film surface by two liquids (water and ethylene glycol) the two components of the free surface energy were calculated by solving the two-equation system.[20] Average (n=5) static contact angle values were considered to evaluate free surface energy. The obtained values are presented in table 2.

Table 2

The free surface energy values determined on the basis of static contact angle

Polymer	Free surface energy[a], mN/m		
	γ_s^d	γ_s^p	γ_s
4a	2.6	41.9	44.5
4b	7.5	25.5	33.0

[a] Based on Owens and Wendt equation[19] by considering the static contact angle values.[20]

As was expected the presence of the fluorine atoms in the poly(ether-imide) structure lead to the lowering free surface energy or the film surface. In the both cases the polar component was majority as compared with dispersive component. This permits to conclude that for the both investigated films the dipole forces and hydrogen-bond effects were important.

Another surface property of interest is the sorption - the process of interaction between the solute and the surface of an adsorbent. The forces involved can be strong (for example, hydrogen bonds) or weak (van der Waals forces). Water vapors uptaking capacity for the three samples at 25°C in the relative humidity range (RH) 0-90% was investigated by using the IGAsorp equipment. The vapors pressure was increased in 10% humidity steps, every having a pre-established equilibrium time between 30 and 40 minutes (minimum time and time out, respectively). At each step, the weight gained was measured by electromagnetic compensation between tare and sample when equilibrium is reached. An anti-condensation system was available for vapor pressure very close to saturation. The cycle was ended by decreasing the vapor pressure in steps to obtain also the desorption isotherms. The drying of the samples before sorption measurements was carried out at 25°C in flowing nitrogen (250 ml/min) until the weight of the sample was in equilibrium at RH<1%. The sorption/desorption isotherms are presented in figure 2.

It is known that the isotherm shapes are mainly determined by the adsorption mechanism, and thus they can be used to explain the nature of adsorption. The isotherms of our samples showing concavities with respect to the relative humidity axis can be associated to those of type III, according to IUPAC classification.[21,22] This type was typical of vapor adsorption (i.e. water vapor on hydrophobic materials), describing macroporous adsorbent with weak adsorbate-adsorbent interactions. However, due to the presence of the hysteresis loop, the isotherms can also be associated with type V that indicates the capillary condensation of the adsorbate in the mesopores of the solid.

It would be expected that the perfluorination of CH_3 groups to increase the hydrophobicity due to the water-repellant effect of fluorine as proved by contact angles measurements (Table 1) and free surface energy determination (Table 2). However, the maximum weight change values at 90% relative humidity (Table 3) indicate a higher weight change in the case of the fluorine-containing sample **4b** (1.685%), as compared with **4a** (1.385%).

This unexpected behavior for the compound containing fluorine **4b** can be explained by low molecular interaction and steric effect induced by CF_3 groups, which hinder the close packing of polymer chains resulting in an increase in free volume and thus facilitating uptake of individual water molecules. More, using a relaxed time regime, the water plasticizes the polymers as it is sorbed, thus facilitating a higher sorption.[23] As can be seen in figure 2, the rate of water desorption was slower as compared with the sorption rate resulting in hysteresis. The hysteresis was attributed to clustering of water molecules. These clusters are less mobile than individual molecules, so desorption was slower.[23]

The glass transition temperature (T_g) values of the polymers **4a** and **4b**, evaluated from DSC curve, were 188°C and 197°C, respectively (Table 4). As it can be seen the introduction of 6F groups instead of isopropylidene groups increases the glass transition temperature.
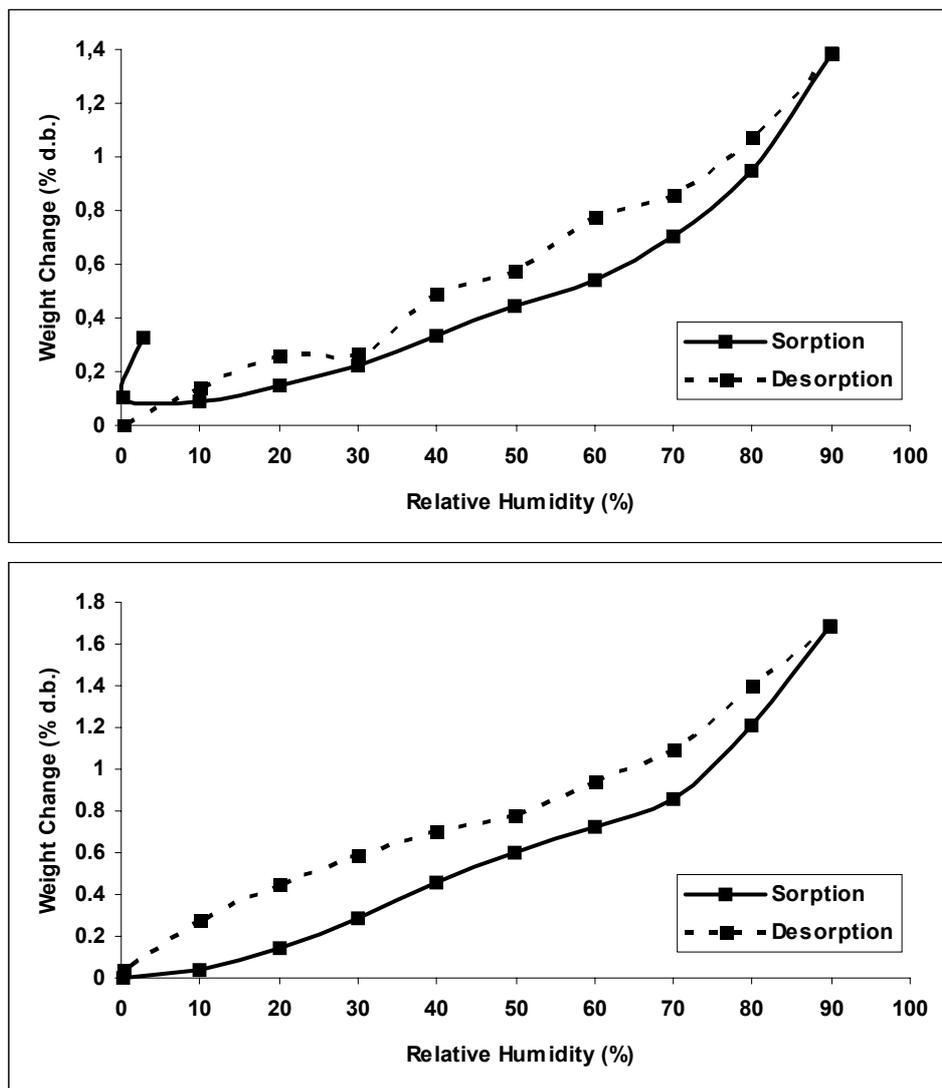
Fig. 2 – Sorption isotherms for the samples 4a (top) and 4b (bottom).

Table 3

Maximum water vapor sorption values

Polymer	Weight change, % (Total water adsorption at RH=90%, T=25°C)
4a	1.385
4b	1.685

Table 4

Thermal properties of polymers **4**

Polymer	T_g^{a}, °C	T_5^{b}, °C	T_{10}^{c}, °C
4a	188	440	500
4b	197	500	530

[a] Glass transition temperature, determined from DSC curves; [b] Initial decomposition temperature = the temperature of 5% weight loss; [c] Temperature of 10% weight loss.

The thermal stability was investigated by thermo-gravimetric analysis. The poly(ether imide)s **4** exhibited high thermal stability, with insignificant weight loss up to 430°C. They lost 5% weight in the range of

440-500°C and the temperature of 10% weight loss (T_{10}) was in the range of 500-530°C (Table 4). Polymer **4b** containing 6F groups exhibited higher thermal stability when compared with polymer **4a** because, at high temperature, the 6F groups are less sensitive then isopropylidene groups.

EXPERIMENTAL

Materials

NMP was purified by stirring with NaOH and distilled from P_2O_5 under reduced pressure. 2,2-Bis[(3,4-dicarboxyphenoxy) phenyl]propane dianhydride, **1a**, 4,4′-(1,3-phenylenedioxy)dianiline, **2**, and all the other reagents were obtained from Aldrich and used as received. 1,1,1,3,3,3-Hexafluoro-2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride, **1b**, has been prepared by a multistep reaction, starting with the nitro displacement reaction of 4-nitro-phthalodinitrile with hexafluoroisopropylidene-bisphenol, in the presence of K_2CO_3.[16] The resulting bis(ether-dinitrile) was subsequently hydrolysed in an alkaline solution and acidified to yield the tetracarboxylic acid, which was then dehydrated in refluxing acetic anhydride to afford the corresponding dianhydride; mp: 229-231°C.

Synthesis of the polymers

The synthesis of poly(ether imide)s **4** took place in two steps (Scheme 1). In the first step poly(amic acid) intermediates **3** were synthesized by the reaction of bis(ether anhydride)s **1** with aromatic diamine **2**, at room temperature, in NMP as solvent, at a concentration of 10-15%. The resulting viscous solutions of poly(amic acid)s were cast onto glass plates followed by evaporating the solvent and thermal imidization at 120°C, 140°C, 160°C, 180°C, 250°C, each for 1 h. Flexible transparent films of poly(ether imide)s **4** were obtained, which were stripped off the plate by immersion in hot water for 2 h. Such films having a thickness in the range of 40-60 μm were dried under vacuum at 100°C and used for different measurements.

Measurements

Infrared spectra were recorded on a FT-IR Bruker Vertex 70 analyzer, by using KBr pellets.

^{1}H NMR spectra were recorded on a Bruker AC 300 instrument, by using solutions in deuterated chloroform.

Water vapors sorption capacity of the samples has been measured by using the fully automated gravimetric analyzer IGAsorp supplied by Hiden Analytical, Warrington (UK). An ultrasensitive microbalance measures the weight change as the humidity is modified in the sample chamber at a constant regulated temperature. System measurements are fully automated and controlled by a user-friendly software package running on Microsoft® Windows[TM].

Dynamic contact angles (DCA) and contact angle hysteresis were measured by using a Sigma 700 tensiometer system - a modular high performance computer controlled (running by a Windows TM software) surface tension/contact angle meter. Static contact angles were measured by the drop technique at room temperature, using a KSV CAM 101 goniometer equipped with a special optical system and a CCD camera connected to a computer to capture and analyze the contact angle (five measurements for each surface).

Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 10°C/min. The initial decomposition temperature is characterized as the temperature at which the sample achieves a 5% weight loss. The temperature of 10% weight loss (T_{10}) was also recorded.

The glass transition temperature (T_g) of the precipitated polymers was determined with a Mettler differential scanning calorimeter DSC 12E, at a heating rate of 10°C/min, under nitrogen.

CONCLUSIONS

Two poly(ether imide)s were prepared starting from an aromatic diamine containing ether linkages and two bis(ether anhydride)s having isopropylidene or hexafluoroisopropylidene groups. They could be easily processed into thin films by solution casting technique. The polymer films having the thickness in the range of tens of micrometers were flexible and resistant. The presence of hexafluoroisopropylidene groups by comparing with isopropylidene groups increased the water dynamic and static contact angles and decreased the free surface energy of the polymer films. Also the hexafluoroisopropylidene groups increased the glass transition temperature and thermal stability .

REFERENCES

1. C. E. Sroog, *Prog. Polym. Sci.*, **1991**, *16*, 561-694.
2. M. Sato, in *Handbook of Thermoplastics*, Olabisi, O., (Ed.), Marcel Dekker: New York, **1997**, p. 665-699.
3. S. J. Huang and A. E. Hoyt, *Trends Polym. Sci.,* **1995**, *3*, 262-271.
4. J. De Abajo and J. G. de la Campa, *Adv. Polym. Sci.,* **1999**, *140*, 23-59.
5. Y. Li, M. Ding and J. Xu, *Polym. Int.,* **1996**, *40*, 57-62.
6. C. P. Yang and C. W. Yu, *J. Polym. Sci.: Part A: Polym. Chem.,* **2001**, *39*, 788-799.
7. D. J. Liaw, C. Y. Hsu, P. N. Hsu and S. Lin, *J. Polym. Sci.: Part A: Polym. Chem.,* **2002**, *40*, 2066-2074.
8. P. V. Buzin, M. Y. Yablokova, A. A. Kuznetsov, A. V. Smirnov and I. G. Abramov, *High. Perform. Polym.,* **2004**, *16*, 505-514.
9. E. Hamciuc and C.Hamciuc*, in Functional Heterochain Polymers* Cazacu M, (Ed.), Nova Science Publishers, Inc., New York, **2008**, p. 187-228.
10. C. Hamciuc, E. Hamciuc, M. Cazacu and L. Okrasa, *Polym. Bull.,* **2008**, *59*, 825-832.
11. R. H. Vora, S. H. Goh and T. S. Chung, *Polym. Eng. Sci.,* **2000**, *40*, 1318-1329.
12. G. Maier, *Prog. Polym. Sci.,* **2001**, *26*, 3-65.

13. E. Hamciuc, C. Hamciuc, I. Sava and M. Brumă, *Eur. Polym. J.,* **2001**, *37*, 287-293.
14. S. H. Hsiao, C. P. Yang and S.C. Huang, *Eur. Polym. J.,* **2004**, *40*, 1063-1074.
15. E. Hamciuc, C. Hamciuc, M. Cazacu, G. Lisa and L. Okrasa, *J. Macromol. Sci. Part A: Pure Appl. Chem.,* **2007**, *44*, 1069-1078.
16. C. Hamciuc, E. Hamciuc and M. Brumă, *Polymer,* **2005**, *46*, 5851-5859.
17. M. Larhrafi, A. Mas, N. Toreis, H. Blancou and F. Schue, *Polym. Int.,* **2003**, *52*, 1795-1798.
18. K. Y. Yeh, L. J. Chen and J. Y. Chang, *Langmuir,* **2008**, *24*, 245-251.
19. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.,* **1969**, *13*, 1741-1747.
20. C. Della Volpe, D. Maniglio, S. Siboni and M. Morra, *Oil & Gas Science and Technology – Rev. IFP*, **2001**, *56*, 9-22.
21. V. Detallante, D. Langevin, C. Chappey, M. Metayer, R. Mercier and M. Pineri, *J. Membr. Sci.,* **2001**, *190*, 227–241.
22. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.,* **1985**, *57*, 603–619.
23. V. Dubey, S. Kuthe, C. Saxena and D. K. Jaiswal, *J. Appl. Polym. Sci.,* **2003**, *88*, 1760-1767.