Polymer Bulletin 59, 825–832 (2008)
DOI 10.1007/s00289-007-0820-7

Polymer Bulletin

Poly(ether-imide) and poly(ether-imide)-polydimethylsiloxane containing isopropylidene groups

Corneliu Hamciuc [1] (✉), Elena Hamciuc [1], Maria Cazacu [1] and Lidia Okrasa [2,3]

[1] "Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 700487 Iasi, Romania
[2] Department of Molecular Physics, Technical University of Lodz, 90-924 Lodz, Poland
[3] Ingénierie des Matériaux Polymères, UMR CNRS 5627, Université Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France

E-mail: chamciuc@icmpp.ro; Fax: (40) 32-211299

Received: 17 June 2007 / Revised version: 22 July 2007 / Accepted: 11 August 2007

Summary

A poly(ether-imide) was prepared by thermal imidization of poly(amic-acid) intermediate resulting from the solution polycondensation reaction of a bis(ether-anhydride), namely 2,2′-bis-[(3,4-dicarboxyphenoxy)phenyl]-1,4-phenylene-diisopropylidene dianhydride, with an aromatic diamine containing two isopropylidene groups, namely 4,4′-(1,4-phenylenediisopropylidene)bisaniline. A poly(ether-imide)-polydimethylsiloxane copolymer was prepared by polycondensation reaction of the same bis(ether-anhydride) with an equimolar quantity of the aromatic diamine having isopropylidene groups and a bis(aminopropyl)polydimethylsiloxane oligomer of controlled molecular weight. A solution imidization procedure was used to convert quantitatively the poly(amic-acid) intermediates to the corresponding polyimides. The polymers were easily soluble in polar organic solvents and showed good thermal stability with decomposition temperature being above 400°C. Electrical insulating properties of poly(ether-imide)-polydimethylsiloxane copolymer film were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency and temperature.

Keywords

poly(ether-imide)-polydimethylsiloxane copolymer; good solubility; thermal stability; thin films; dielectric constant

Introduction

High performance polymer films and coating materials are increasingly being required by the electronics industry for use as interlayer dielectrics and passivation coatings in integrated circuit fabrication. For optimum performance the dielectrics used in these devices should display excellent thermal and chemical resistance, low moisture absorption and a dielectric constant value as low as possible [1]. Aromatic polyimides are generally the polymers of choice for these applications due to their unique combination of chemical, physical and mechanical properties [2, 3]. However, these polymers are processed with great difficulty because many of them are insoluble and infusible. Various efforts have been made on the synthesis of soluble and processable polyimides without much sacrifice of their excellent thermostability. The introduction of kinks or flexible linkages, noncoplanar units or bulky lateral groups along the backbone was used to improve the solubility of these polymers [4, 5]. It has been generally recognized that aromatic ether linkages or isopropylidene groups inserted in aromatic main chains provide them with a significantly lower energy of internal rotation. In general, such a structural modification leads to lower glass transition temperature and crystalline melting temperatures as well as significant improvement in solubility and other processing characteristics [5, 6]. Also, the incorporation of polydimethylsiloxane sequences in polyimides has afforded new copolymers with good processability, low water absorption, atomic oxygen resistance and excellent adhesion. The unique properties of the imide siloxane copolymeric materials make them especially attractive for applications in microelectronics and as structural adhesives. The introduction of non-polar monomers is capable to obtain polyimide systems with lower dielectric constant than classical aromatic polyimides [7-13].

In this article we report the synthesis of a poly(ether-imide) and a poly(ether-imide)-polydimethylsiloxane copolymer containing isopropylidene groups. The properties of these polymers, such as solubility, thermal stability, glass transition temperature, film forming as well as the electrical characteristics, have been evaluated with respect to their chemical structure.

Experimental

Instrumental

Infrared spectra were recorded with a Specord M80 spectrometer by using KBr pellets. ^{1}H-NMR spectra were recorded using a Bruker Avance DRX 400, at room temperature. The molecular weight distributions were measured by gel permeation chromatography with a PL-EMD 950 evaporative mass detector instrument. Polystyrene standards of known molecular weight were used for calibration. 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. Thermogravimetric analysis (TGA) was performed using a MOM Derivatograph (Hungary) in air, at a heating rate of 10°C/min. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieved a 5% weight loss. The dielectric measurements were carried out using a Novocontrol system composed from an Alpha frequency response analyzer and Quattro temperature controller. The sample was prepared in the form of film with thickness of about 0.1 mm with gold electrodes evaporated in vacuum and placed inside temperature controlled sample cell. The complex permittivity: $\varepsilon^*(f) = \varepsilon'(f) + i\varepsilon''(f)$ has been determined in the frequency (f) range from 10^{-1} Hz to 10^6 Hz and at temperature range from -100° to 200°C. The AC voltage applied to the capacitor was equal to 1.5 V. Temperature was controlled using a nitrogen gas cryostat and the temperature stability of the sample was better than 0.1°C. The samples where sandwiched between two copper electrodes of diameter 20 mm. Dielectric results were presented in the classical representation of complex dielectric permittivity ($\varepsilon^* = \varepsilon' + i\varepsilon''$), as well as using the electric modulus ($M^* = M' + iM''$) representation defined by Macedo et al. [14]. The real M' and imaginary M'' parts of the electric modulus were calculated according to the equations:

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \; ; \; M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$$

where: ε' and ε'' are respectively real and imaginary part of the permittivity.

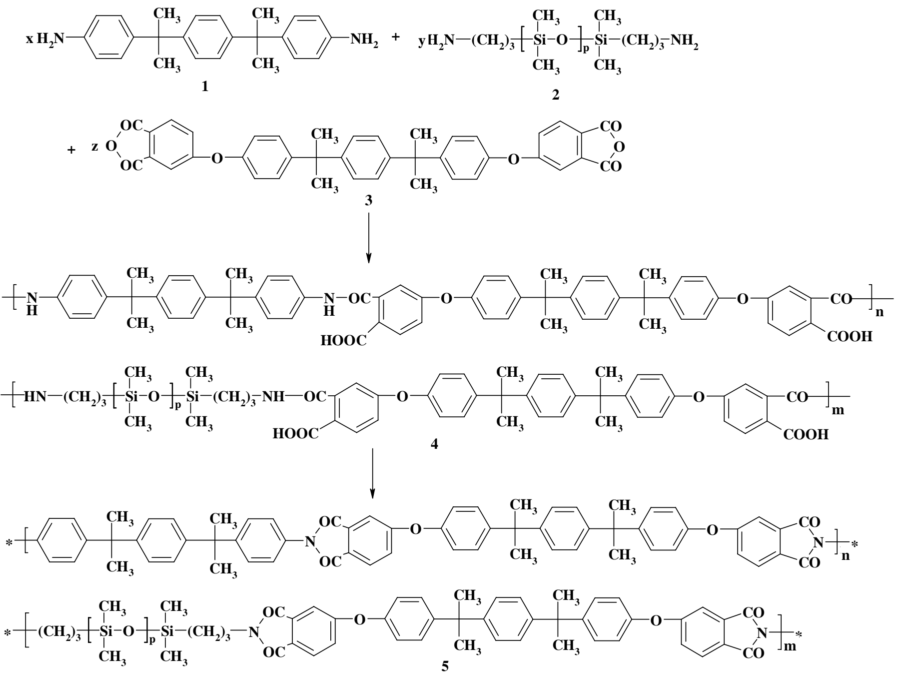
Synthesis of the monomers

The α,ω-(3-aminopropyl)oligodimethylsiloxane, **2**, was synthesized by equilibration of the cyclic siloxane tetramer, $[(CH_3)_2SiO]_4$ (octamethylcyclotetrasiloxane), with 1,3-bis(3-aminopropyl)tetramethyldisiloxane, in a pre-established ratio to obtain the desired molecular weight. A base, tetramethylammonium hydroxide was used as a catalyst [15]. The average numerical molecular weight of the resulted oligomer as determined on the basis of ^{1}H-NMR spectrum was 1120 g/mol. IR (KBr, cm^{-1}): 805, 1260 (Si-CH_3), 1069 (Si-O-Si), 1571 (N-H bending), 1486 (C-NH_2), 2962 (C-H), 3302 (NH_2). ^{1}H-NMR ($CDCl_3$, ppm): δ = 0.04-0.07 (Si-$(C\underline{H}_3)_2$), 0.49-0.54 (Si-$C\underline{H}_2$-CH_2-CH_2-NH_2), 1.24 (Si-CH_2-CH_2-CH_2-$N\underline{H}_2$), 1.41-1.49 (Si-CH_2-$C\underline{H}_2$-CH_2-NH_2), 2.63-2.67 (Si-CH_2-CH_2-$C\underline{H}_2$-NH_2).

2,2′-Bis-[(3,4-dicarboxyphenoxy)phenyl]-1,4-phenylenediisopropylidene dianhydride **3** [16], was prepared by a multistep reaction, starting with the nitro displacement reaction of 4-nitro-phtalodinitrile with 4,4′-(1,4-phenylene-diisopropylidene)-bisphenol. (Yield: 70%). Mp:190-192°C. IR (KBr, cm^{-1}): 1860 and 1780 (C=O), 2980 (CH_3), 1240 (C-O-C) . ^{1}H-NMR (DMSO-d_6, ppm): δ = 8.1 (2H, d), 7.53 (2H, d), 7.40 (2H, d), 7.34 (4H, m), 7.20 (8H, m), 1.67 (12H, s).

*Synthesis of the polymers **4** and **5***

The synthesis of the polymers **4** and **5** is depicted in scheme 1. The poly(amic-acid) intermediate **4a** was synthesized by slowly adding the solid dianhydride **3** to a stirring solution of the diamine **1**. The reaction was conducted at room temperature, under a nitrogen atmosphere, in N-methylpyrrolidone (NMP). The polymer solution was heated at 180-185°C for 4 h, under a nitrogen stream, to perform the cyclization of the poly(amic-acid) **4a** to the corresponding polyimide structure **5a**, according to a method previously described [17]. The siloxane-containing poly(amic-acid) intermediate **4b** was obtained as is described in the following example. To a solution of the dianhydride **3** (0.638 g, 1 mmol) in 3 ml of NMP/tetrahydrofuran (THF) (1:1) an amine – terminated polydimethylsiloxane oligomer **2** (0.560 g, 0.5 mmol) solution in 2 ml of THF was added slowly at room temperature. After the mixture was stirred for 1 h, diamine **1** (0.126 g, 0.5 mmol) in 2 ml NMP was added, and the mixture was stirred at room temperature for 10 h. The yellow, viscous solution that was obtained was imidized by heating in a mixture of *m*-xylene/NMP (2/5, v/v) at reflux temperature, for 4 h. The xylene was distilled off under vacuum and the resulting solution was precipitated in a large quantity of water to give a yellow-brown rubbery material, **5b**, which was dried in vacuum at 80ºC, for 24 h. The yield of the reaction was 85%. Films of polymers **5** were prepared by casting a solution of 5% concentration of polymer in chloroform onto glass plates, followed by drying at room temperature for 24 h under a Petri dish and for another 2 h at 130°C [18]. Films obtained from polymer **5a** were brittle, while the films obtained from copolymer containing siloxane sequences **5b** were flexible.



4a, 5a: x=z, y=0 ; **4b, 5b**: x=y=0.5, z=1

Scheme 1. Synthesis of the polymers **4** and **5**.

Results and discussion

The structure of the polymers was confirmed by IR and ^{1}H-NMR spectroscopy. In IR spectra of polymers **5** strong bands appearing at 1780 cm^{-1}, 1720 cm^{-1}, 1390 cm^{-1} and 740 cm^{-1} were due to imide rings. The absorption peak at 1230 cm^{-1} was assigned to the aromatic ether Ar-O-Ar. The polymers **4** and **5** showed characteristic absorption bands at 2970 cm^{-1} and 2870 cm^{-1} due to asymmetric and symmetric stretching of methyl groups. In the IR spectra of polymers **4b** and **5b** the presence of siloxane units was evidenced by the characteristic absorption bands at 1080 cm^{-1} (Si-O-Si) and 800 cm^{-1} (H_3C-Si). In ^{1}H-NMR spectrum of polymer **5b** the peaks corresponding to the aromatic protons were centered in the interval of 7.9-6.8 ppm. The spectrum showed a characteristic peak at 3.7 ppm corresponding to the protons of the methylene group adjacent to the terminated imide ring. The characteristic peaks corresponding to the other protons of methylene groups appeared at 1.8 ppm and 0.6 ppm. The protons of isopropylidene groups appeared at 1.8 ppm.

The polyimides **5** were soluble in polar solvents such as NMP, N,N-dimethylacetamide, chloroform and tetrahydrofuran. The good solubility allowed the imidization process to be performed in solution so that the final polymer was obtained as an imidized product, which is more convenient than using poly(amic acid). The solubility of the present polyimides is explained by the presence of flexible bridges such as ether and isopropylidene. In the case of polymer **5b** the good solubility can be explained by the presence of polydimethylsiloxane segments which improve the flexibility of the macromolecular chains thus improving the solubility.

The values of weight-average molecular weight of the polymers **5** (*Mw*) were in the range of 34000-44000 g/mol and the number-average molecular weight (*Mn*) was in the range of 12500-17400 g/mol (Table 1).

The polymers did not show significant weight loss below 400°C. They began to decompose in the range of 415-490°C; they showed 10% weight loss in the range of 445-500°C. The degradation process of polymers **5** exhibited two maxima of decomposition. The first (T_{max1}) was in the range of 500-515°C and was probably due to the destruction of methylene groups. The second maximum of the decomposition (T_{max2}) was in the range of 650-670°C and was due to the degradation of polymer chain itself (Table 1). The polymer **5a** without polysiloxane segments exhibited higher thermal stability.

Table 1. The properties of polymers **5**.

Polymer	Mn (g/mol)	Mw (g/mol)	T_g[1] (°C)	IDT[2] (°C)	T_{10}[3] (°C)	T_{max1}[4] (°C)	T_{max2}[5] (°C)
5a	12500	34000	149	490	500	500	670
5b	17400	44000	-	415	445	515	650

[1] Glass transition temperature, from DSC curves; [2] Temperature of 5% weight loss;
[3] Temperature of 10% weight loss; [4] First maximum polymer decomposition temperature;
[5] Second maximum polymer decomposition temperature.

The glass transition temperature of the polymer **5a**, evaluated from DSC curve, was 149°C (Table 1). It can be noticed that there is a large interval between the glass transition and decomposition temperature which makes this polymer attractive for thermoforming processing. No transitions were observed for polymer **5b** containing siloxane sequences by DSC analysis from -150°C to 300°C.

Electrical insulating properties of polymer film **5b** were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency and temperature [19-21]. The dielectric permittivity of a material is, in general, a complex quantity, when measured in the frequency domain.

Figures 1 and 2 present the dependence of real and imaginary parts of complex permittivity on frequency, for polymer **5b** at different temperatures taken in the range from -100°C to 180°C. The dielectric constant (ε') increased with decreasing of frequency as well as with increasing of temperature. From figure 2 it can be seen that ε' slightly decreases with increasing frequency at low (-100°C) and moderate (20°C) temperature. An increase of ε' can be observed at high temperature. This behavior can be attributed to the frequency dependence of the polarization mechanisms, which comprise the dielectric constant. The magnitude of the dielectric constant is dependent upon the ability of the polarizable units to orient fast enough to keep up with the oscillations of the alternating electric field [22]. For many applications, dielectric materials with stable dielectric constant and dissipation factor values across large frequency and temperature range are highly preferred.

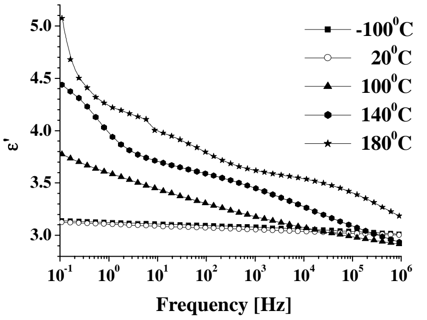


Figure 1. Dependence of dielectric constant (ε') versus frequency at different temperatures, for polymer **5b**.

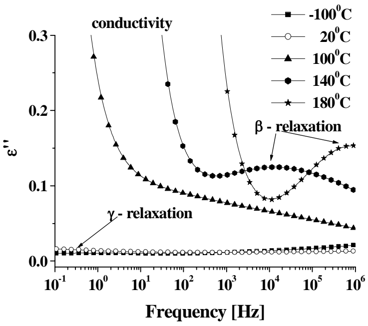


Figure 2. Dependence of dielectric loss (ε'') versus frequency at different temperatures, for polymer **5b**.

The dielectric constant values at 100 Hz, 10 kHz and 1 MHz at room temperature were 3.06, 3.03 and 3.00, respectively. It can be seen that the dielectric constant at 10 kHz is lower in comparison with that of H Film - a polyimide, which is one of the most common polyimides used as dielectric in microelectronics applications, having a dielectric constant of 3.5 [2]. This can be probably explained by the presence in the main chains of non-polar polysiloxane sequences and bulky $C(CH_3)_2$ groups, which reduced the humidity absorption and increase free volume and thus lowering the polarization by decreasing the number of polarizable groups per unit volume.

The dielectric loss for polymer film **5b** at different temperatures taken in the range from –100°C to 180°C is shown in figure 2. The dielectric loss showed similar dependence on frequency. At moderate temperature the dielectric loss exhibited low values in the interval of measured frequency. Low values of the dielectric loss are indicative of minimal conversion of electrical energy to heat in the dielectric material. It is advantageous to have low values for both dielectric constant and dielectric loss because electrical signals will loss less of their intensity in the dielectric medium. At 180°C and low frequency it can be observed an increase of ε' and a sharp increase of ε''. The strong low-frequency dispersion for ε' and sharp increasing of ε'' are the characteristics of charge carrier systems. The localized charge carriers under an applied alternating electric field can hop to neighboring localized sites like the reciprocating motion of a jumping dipole or can jump to neighboring sites, which form a continuous connected network allowing the charges to travel through the entire physical dimensions of the polymer sample and causing the electric conduction. During the motion of charge carriers, the applied electric field will be a subject of decay. Such relaxation of electric field is termed electric field relaxation and the relaxation of the charge system is termed conductivity relaxation [23].

For the dielectric loss ε'' it can be seen two secondary relaxations (β and γ) connected with local movements of polymer chains. The γ relaxation could be in the same region with α transition of polysiloxane segments. However, the transition at low temperature (-100°C) was very week suggesting a partially phase mixing of the polyimide and polysiloxane segments. The origin of the β relaxation is not clear. The most probably is associated with phenyl ring motions. Then the conductivity process arises and masks the primary relaxation connected with the upper glass transition, which should have place at higher temperature.

In order to analyze the conductivity relaxation of the polymer film, the complex permittivity was converted to the complex dielectric modulus. The frequency dependencies of the real (M') and imaginary (M'') parts of the dielectric modulus for polymer **5b** are shown in figure 3, as determined for different temperatures.

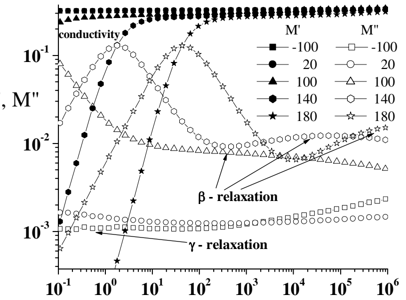


Figure 3. Dependence of real and imaginary parts of complex dielectric modulus versus frequency, at different temperatures, for polymer **5b**.

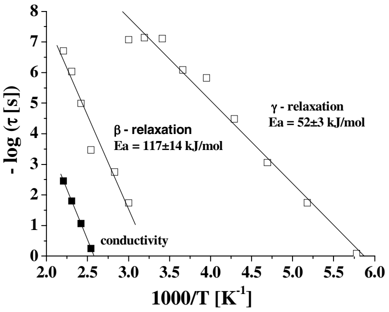


Figure 4. Activation maps for polymer **5b**. Open points are taken from positions of the ε'' *(f)* maxima and full points are taken from positions of the M'' *(f)* maxima.

The dispersions of M' and M''indicate a presence of relaxation time of distribution of conduction. We can observe three relaxation processes. The first two, γ and β, are the secondary relaxations connected with local movements and were also observed in the dependence of $\varepsilon''$with frequency. Last one is the conductivity process which masks the primary relaxation connected with glass transition and partially also the β relaxation process. The activation map is the best way for a comparison of the relaxation processes as well as is necessary for calculation of their activation energy. Relaxation times (τ) of the secondary relaxation processes at various temperatures have been determined from maxima position of ε''at frequency scale. The activation plots are shown in figure 4. In figure 4 also the activation energies of the β and γ relaxation processes calculated on the bases of these diagrams are presented. Relaxation times of the conductivity processes at various temperatures have been determined from maxima position of M''at frequency scale.

Conclusions

The introduction 1,4-phenylenediisopropylidene units into the macromolecular chain of a poly(ether-imide) resulted in soluble polymers that retain a high thermal stability. Also the incorporation of polysiloxane segments into their structure produced a polymer with good solubility in organic solvents while retaining high thermal stability. Poly(ether-imide)-polydimethylsiloxane copolymer film has low dielectric constant, which makes it potential candidate for future high performance applications in microelectronics or in related fields.

Acknowledgements. This research has been occurred in the frame of Project CEEX-MATNANTECH No. 97/2006. The dielectric investigations were supported by EU project "DIELPOL" N° MTKD-CT-2005-029670.

References

1. Maier G (2001) Prog Polym Sci 26: 65
2. Sroog CE (1991) Prog Polym Sci 16: 561
3. Hasegawa M, Horie K (2001) Prog Polym Sci 26: 259
4. Huang SJ, Hoyt AE (1995) Trends Polym Sci 3: 262
5. de Abajo J, de la Campa JG (1999) Adv Polym Sci 140: 23
6. Hamciuc C, Hamciuc E, Bruma M (2005) Polymer 46: 5851
7. Furukawa N, Yuasa M, Kimura Y (1998) J Polym Sci: Part A: Polym Chem 36: 2237
8. Andre S, Guida-Pietrasanta F, Rousseau A, Boutevin B (2001) J Polym Sci: Part A: Polym Chem 39: 2414
9. Mahoney CM, Gardella Jr JA, Rosenfeld JC (2002) Macromolecules 35: 5256
10. Racles C, Cozan V, Cazacu M, Foldes E, Sajo I (2002) High Perform Polym 14: 397
11. Krea M, Roizard D, Moulai-Mostefa N, Sacco D (2004) J Memb Sci 241: 55
12. Simionescu M, Sacarescu L, Ardeleanu R, Sacarescu G (2005) High Perform Polym 17: 73
13. Andre S, Guida-Pietrasanta F, Rousseau A, Boutevin B, Caporicco G (2005) J Polym Sci: Part A : Polym Chem 43: 2237
14. Macedo PB, Moynihan CT, Bose R, (1972) Phys Chem Glasses **13**: 171
15. Cazacu M, Vlad A, Simionescu M, Racles C, Marcu M (2002) J Macromol Sci-Pure and Appl Chem 39: 1487
16. Eastmond GC, Paprotny J, Webster I (1993) Polymer 34: 2865
17. Hamciuc E, Hamciuc C, Bruma M, Schulz B (2005) Eur Polym J 41: 2989
18. Hamciuc C, Hamciuc E, Bruma M, Klapper K, Pakula T, Demeter A (2001) Polymer 42: 5956
19. Sava I, Iosip MD, Bruma M, Hamciuc C, Robison J, Okrasa L, Pakula T (2003) Eur Polym J 39: 725
20. Hamciuc C, Hamciuc E, Pakula T, Okrasa L (2006) J Appl Polym Sci 102:3062
21. Hamciuc C, Hamciuc E, Pakula T, Okrasa L (2006) Polym Plast Tech Eng 45: 143
22. Deligoz H, Yalcinyuva T, Ozgumus S, Yildirim S (2006) J Appl Polym Sci 100 : 810
23. Lee HT, Chuang KR, Chen SA, Wei PK, Hsu JH, Fann W (1995) Macromolecules 28: 7645