

Effect of Molecular Structures on Polyimide Properties: Comparison between Estimations and Experiments

Yexin Xu,¹ Cuixian Chen,¹ Pengxia Zhang,² Benhui Sun,² Jiding Li¹

¹Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

²School of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Received 8 March 2006; accepted 1 May 2006

DOI 10.1002/app.25289

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The density and glass transition temperature (T_g) of 11 polyimides were investigated by experiments and predictions using the connectivity indices method to explore the structure–property relationships. The predicted results are in good agreement with the experimental data. The mean interchain spacings (d -spacings) of polyimides increase with the introduction of bridging groups, i.e., following the order: PDA < BZD < ODA < MDA < BDAF, while the densities increase in the order of MDA < BZD < PDA, and cohesive energy densities (CEDs) of polyimides change following the order of BDAF < MDA < ODA

< BZD < PDA. In addition, the glass transition temperatures (T_g 's) increase as the CEDs increase for the polyimides prepared from the same dianhydride and different diamines, whereas no certain correlation exists between T_g 's and the values of the characteristic ratio (C_∞). This indicates that the strength of interchain interaction influences the T_g 's of polyimides much stronger than the chain flexibility. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 998–1003, 2007

Key words: polyimides; connectivity indices method; glass transition temperature; membranes; density

INTRODUCTION

In the past decade, polyimides have been widely used in applications such as aircraft parts, electronic packaging, membranes, adhesives, and matrix materials for composites because of their good thermal stability, excellent mechanical, electrical, and solvent-resistance properties. However, their properties are mostly determined by their molecular structures, which relate to the monomer structures used in the polymerization. Thereby, a slight modification of the chemical structure may often result in a significant change in material's properties. Some investigators have studied the relationships between monomer structure and polyimide property.^{1,2} However, considering the experimental condition limitation, it is unadvisable and uneconomical to synthesize all the possible structures of polyimides. Consequently, several estimation methods have been developed to assess polymeric materi-

als in an attempt to predict their macroscopic and microscopic properties such as the T_g , density, conformation, and chain orientation.

Of the estimation and correlation methods, the group-contribution method³ is the most commonly used one. It is usually based on the assumption that the structural groups in the repeating units provide a weighted additive contribution to the polymer's properties. This method is of greatest utility when a rapid estimate of a property is required without a detailed understanding of the atomistic interactions. However, the group-contribution approach has some inherent limitations. The most important limitation is its reliance upon a database of group contributions. Consequently, if a polymer contains a group, for which the group contribution cannot be estimated, the property of that polymer cannot be calculated. Lee⁴ made some progress and was able to predict the T_g 's of polyimides with ether linkages or ether equivalence. Nevertheless, he did not provide the parameters for other kinds of polyimides, in which we are interested. Liang et al.⁵ used molecular dynamic simulation with the DREIDING II force field to predict the T_g 's of polyimides by calculating the energy barrier of the bridging bonds between moieties along the main-chain backbone. And the predicted values of T_g 's slightly departed from the experimental results. Damian et al.⁶ also studied the thermal stability of some aromatic polyethers containing a pentamethylene spacer by molecular simulation. Computer-simulated properties of the investigated polymers,

Correspondence to: C. Chen (cxchen@tsinghua.edu.cn).

Contract grant sponsor: Major State Basic Research Program of China (973 Program); contract grant number: 2003CB615701.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20576059.

Contract grant sponsor: SINOPEC; contract grant number: X505002.

Contract grant sponsor: CNPC.

Journal of Applied Polymer Science, Vol. 103, 998–1003 (2007)
© 2006 Wiley Periodicals, Inc.

such as order parameter and polarity of polymers, were all in good agreement with the experimental values. However, Damian did not compare the properties including densities and T_g 's between simulations and experiments.

Bicerano⁷ proposed connectivity indices derived from graph theory as fundamental descriptions of the molecular structure for the repeat unit of a given polymer to predict the properties of polymers. Thus, no database of group contributions is required, and properties may be predicted for any polymer composed of any combination of the following nine elements: carbon, hydrogen, nitrogen, oxygen, silicon, sulfur, fluorine, chlorine, and bromine. In the past, it was shown that connectivity indices approach has some limitations, for example, it cannot be useful at all if rotations take place in the molecular structure. However, some success has been achieved in predicting some properties, for some polymers.⁸ The description of this theory would be summarized in detail later.

In the present study, the densities and T_g 's of polyimides with different structures were predicted with the connectivity indices method. In contrast, these polyimide materials were synthesized using three dianhydrides with five diamines as the monomers. The properties mentioned earlier and the d -spacings were measured by experimental techniques. The relationships between molecular structure and property of polyimide materials were investigated to lay the foundations for the preparation of new materials with excellent performances.

THEORY

Characteristic ratio

The characteristic ratio, C_∞ , is a measure of the intrinsic flexibility and rigidity of a coiled chain, given by eq. (1), where "lim" denotes "limit", n is the number of bonds along the shortest path across the chain backbone, $\langle r^2 \rangle_0$ denotes the mean-square end-to-end distance of an unperturbed linear chain molecule in solution, and n_i is the number of times the i th type of bond, which has a bond length of l_i , occurs along this shortest path.

$$C_\infty \equiv \lim_{n \rightarrow \infty} \left[\frac{\langle r^2 \rangle_0}{\sum (n_i l_i^2)} \right] \quad (1)$$

It can be seen from this definition that the more flexible the polymer chains are, the smaller the C_∞ is.

Cohesive energy density

The cohesive energy, E_{coh} , of a material is the increase in the internal energy per mole of the material if all of its intermolecular forces are eliminated. The total co-

hesive energy, E_{coh} , can be divided formally into three parts, E_d , E_p , and E_h , representing contributions from dispersion, polar, and hydrogen bonding interactions, respectively.

$$E_{\text{coh}} = E_d + E_p + E_h \quad (2)$$

Then, the cohesive energy density (CED) is defined by eq. (3):

$$\text{CED} = E_{\text{coh}}/V_m \quad (3)$$

where V_m is the molar volume of the material.

Connectivity indices method

As mentioned in the introduction, connectivity indices defined via graph theoretical concepts have been widely used for simple molecules.^{9,10} Two atomic indices δ and δ^v are defined to describe the bonding and electronic environment of each nonhydrogen atom. Then, the bond indices β and β^v are both defined for each bond, not involving a hydrogen atom, as products of the atomic indices δ and δ^v . Furthermore, the connectivity indices ω for the entire molecule are defined in terms of the bond indices.

Bicerano⁷ extended the method for simple molecules described earlier to calculate ω values for polymer chains correctly with some modifications. Extensive properties such as molar volume, molar heat capacity, and cohesive energy depend upon the size of the system and their values increase in direct proportion to the amount of materials present. These sorts of properties are correlated directly with the values of ω . On the other hand, intensive properties are essentially independent of the amount of materials present, provided that it is nonzero. These properties are correlated with the values of ω scaled by the number of nonhydrogen atoms in the system. The formulas calculating the density, C_∞ , CED, and T_g were shown in detail elsewhere.⁷

EXPERIMENTAL

Materials

All chemicals were purchased from Acros Organics (Geel, Belgium) and Fluka Chemical Benzidine (BZD) (Fluka Chemical Corp., New York, USA), 4,4'-diaminodiphenylmethane (MDA), 4,4'-diaminodiphenylether (ODA), phenylenediamine (PDA), bis[4-(4'-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (BDAF), 2,2-bis[4-(3,4-dicarboxyphenoxy)-phenyl] propane dianhydride (BPADA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (ODPA) were purified before polymerization. *N,N*-dimethylformamide (DMF)

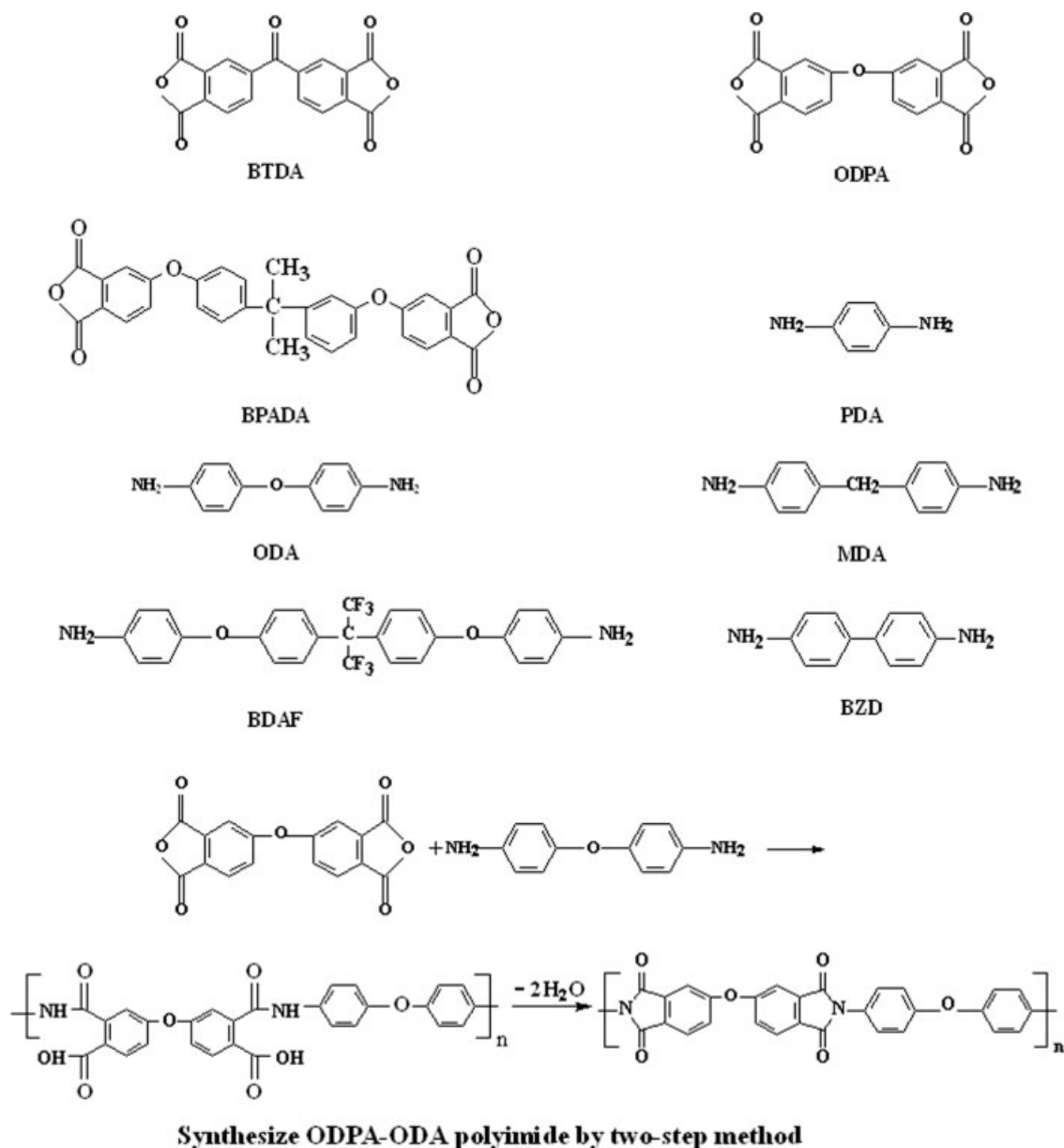


Figure 1 The chemical structures of polyimide monomers.

was purified on distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å).

All the monomers of polyimides are shown in Figure 1, and the structure of ODPA-ODA as an example of polyimide is also shown.

Polyamic acid synthesis and preparation of polyimide membrane

The polyamic acid (PAA) precursors of polyimides were prepared by solution condensation polymerization at ambient temperature and at a concentration of 12% solids by weight in DMF. The aromatic dianhydride monomer was added to an equimolar amount of aromatic diamine dissolved in the solvent.

The polymers used in this study were in the form of membranes. So the obtained PAA solution was cast onto a soda-lime glass plate to form a casting membrane. Then the casting film was placed into a vacuum dryer for 24 h to remove some residual solvent. Thermal conversion of the PAA membranes to the corresponding polyimides was performed by heating in a vacuum oven for 2 h each at 180, 250, and 300°C. Upon cooling, the membranes were removed from the glass plates. Finally, 20–40- μm -thick homogeneous films were obtained.

Characterization

The density of polyimide membranes at 298 K was measured by flotation in a mixed solution. The solu-

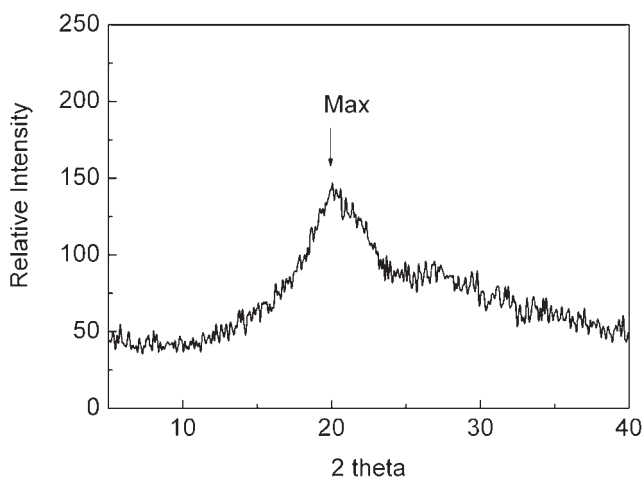


Figure 2 The WAXD pattern of BTDA-ODA polyimide.

tion was prepared by ethanol ($\rho = 0.79 \text{ g/cm}^3$) and carbon tetrachloride ($\rho = 1.599 \text{ g/cm}^3$). The T_g of polyimide was determined by differential scanning calorimetry with a Seiko EXSTAR6000 instrument at a heating rate of 10 K/min, from 298 to 673 K. Wide-angle X-ray diffraction (WAXD) patterns were measured by a Bruker D8 wide angle X-ray diffractometer using Cu K α radiation wavelength, and the WAXD pattern of BTDA-ODA polyimide was displayed in Figure 2. The top of broad peaks on each X-ray pattern for noncrystalline polymers is attributed to intersegmental interference, and is thus a representative of average intersegmental distance called as a d -spacing. The d -spacing can be calculated from Bragg's equation.¹¹

RESULTS AND DISCUSSION

The connectivity indices method was used to estimate the densities, characteristic ratio C_∞ and T_g 's of 11 polyimides, and the values are presented in Tables I and II. In contrast to the d -spacings, densities and T_g 's were measured by experimental techniques, and the values are also presented in Tables I and II.

In the experimental results, most of the d -spacings of polyimides with the same dianhydrides increase in the order of PDA < BZD < ODA < MDA < BDAF, probably due to the introduction of bridging atoms or groups, such as the $-\text{CH}_2-$ and $-\text{C}(\text{CF}_3)_2-$ linkages in the main chain of MDA and BDAF, respectively. The d -spacings of the PDA- and BZD-based polyimides are lower than the others because of their phenyl structure and the lack of bridging atoms, and the d -spacings of ODA- and MDA-based polyimides are higher than the others, because their bridging atoms are bridging oxygen and methylene, respectively. BDAF-based polyimides have the highest value of the d -spacing, approximately, because of

their larger bridging atom groups and the complex structure of BDAF.

As shown in Table I, the values of densities calculated from the connectivity indices method are in good agreement with the experimental data. It is indicated that the connectivity indices method is good for such polyimide structures in predicting the density. Furthermore, it can be observed that with the same dianhydride, the densities of the polyimides decrease in the following order: PDA > BZD > MDA. This suggests that the bulky bridging groups in the main chain act as factors not allowing efficient packing by steric hindrance, thereby increasing the d -spacing and reducing the packing density. The density of BPADA-PDA polyimide is the lowest due to the two methyl groups in the BPADA moieties, which obstruct the packing of chains. However, when the bulky bridging groups include other elements such as O and F, the densities may be influenced not only by steric hindrance but also by other factors. Consequently, the densities of BTDA-ODA and BTDA-BDAF polyimides are larger than that of BTDA-BZD polyimide.

Figures 3 and 4 show the relations of CEDs and d -spacings on BTDA- and ODPA-based polyimides, respectively. It can be seen that the CEDs decrease as the d -spacings increase with the introduction of bridging groups. As mentioned in the introduction, factors included in CED are a dispersion force, a force between permanent dipoles and forces between polar groups, which involve hydrogen bonding. So, as shown in Table II, all the polyimides in this study exhibit high CED, and BDAF-based polyimides show considerably low CED when compared with other polyimides, probably due to the bulky $-\text{CF}_3$ groups. Bulky groups will increase the d -spacings and decrease the interaction.

The data of T_g provided by experiments and predictions using the connectivity indices method are presented in Table II. It is indicated that most of the predicted values of T_g show a good agreement with

TABLE I
Values of d -Spacings and Densities of Polyimides

Polyimide	d -spacing (Å)	Density (g/cm ³)	
		Experimental	Predicted
BPADA-PDA	5.9	1.282	1.279
BTDA-MDA	4.9	1.337	1.342
BTDA-BZD	4.1	1.356	1.361
BTDA-ODA	4.3	1.373	1.372
BTDA-PDA	3.9	1.405	1.412
BTDA-BDAF	5.7	1.401	1.413
ODPA-MDA	4.9	1.326	1.338
ODPA-BZD	4.9	1.354	1.357
ODPA-ODA	5	1.378	1.368
ODPA-PDA	4.5	1.414	1.409
ODPA-BDAF	5.7	1.399	1.411

TABLE II
Values of CEDs and T_g 's of Polyimides

Polyimide	CED (MJ/m ³) predicted	C_∞ predicted	T_g (K)	
			Experimental	Predicted
BPADA-PDA	524	3.386	541	493
BTDA-PDA	659	3.418	581	594
BTDA-BZD	617	3.464	558	578
BTDA-ODA	615	3.382	544	540
BTDA-MDA	604	3.571	531	536
BTDA-BDAF	537	3.433	526	519
ODPA-PDA	617	3.318	584	592
ODPA-BZD	582	3.384	559	576
ODPA-ODA	581	3.305	538	537
ODPA-MDA	570	3.492	534	533
ODPA-BDAF	514	3.377	530	519

the experimental values for polyimides prepared from monomers with simple chemical structure such as BTDA-MDA, BTDA-ODA, and ODPA-MDA polyimides. However, the connectivity indices method is not good for complex polyimide structures such as BPADA-PDA, and the predicted values remarkably depart from the experimental results.

There are many factors affecting T_g 's of polymers. In general, two of the most important factors are the chain flexibility and the strength of interchain interaction,⁵ and to some extent, they can be characterized by the terms of C_∞ and CED, as mentioned in the theory, respectively. As shown in Table II, with the same dianhydrides, T_g 's of different polyimides decrease with the addition of chromophores in the diamine monomers, i.e., following the order of PDA > BZD > ODA > MDA > BDAF, which is the same to the order that the CEDs of polyimides decrease in the following. However, no certain correlation was found between the values of C_∞ and the T_g 's of polyimides from the data in Table II. For example, the T_g 's

of BTDA-based polyimides decrease following the order of PDA > BZD > ODA > MDA > BDAF, while the C_∞ decreases in the order of MDA > BZD > BDAF > PDA > ODA. Consequently, the interchain interaction maybe more important for the T_g 's of the polyimides, in this study, than the chain flexibility. The presence of bridging groups causes a descent of the CEDs of polyimides. So the T_g 's decrease as the CEDs decrease in the polyimides prepared from the same dianhydride and different diamines. The results are in good agreement with the findings of Tang et al.¹²

CONCLUSIONS

The connectivity indices method was applied to predict the densities and T_g 's of 11 polyimides prepared from 3 dianhydrides and 5 diamines. The predicted results indicated a good agreement with the experimental values, except the prediction of T_g for BPADA-PDA polyimide prepared from the monomer possess-

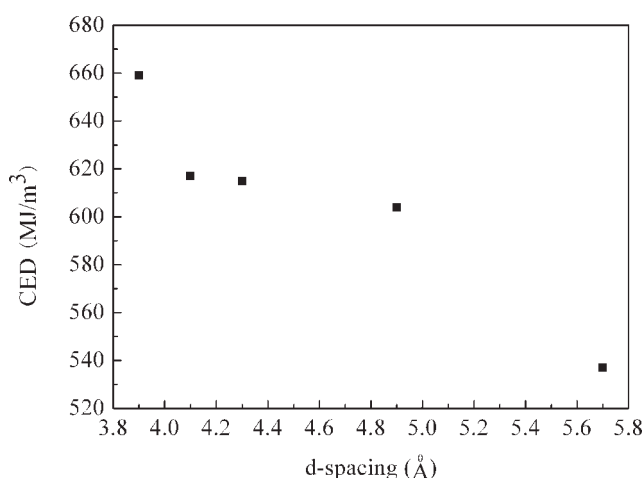


Figure 3 Relation of CED and d -spacing on BTDA-based polyimides.

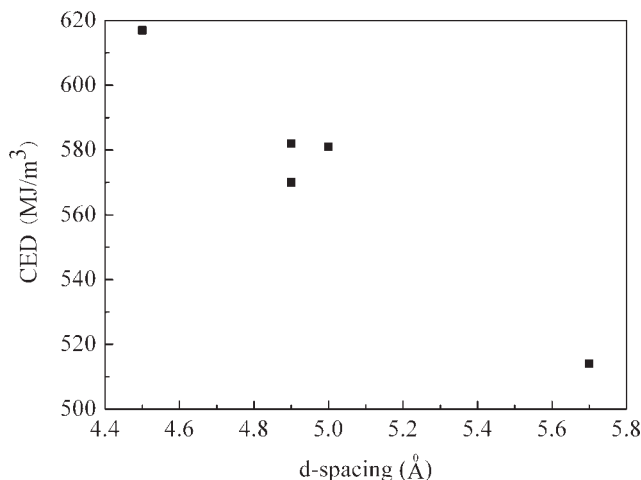


Figure 4 Relation of CED and d -spacing on ODPA-based polyimides.

ing complex chemical structure such as BPADA. It can be concluded that the connectivity index is not suitable for complex polymer structures.

Some structure–property relationships were developed qualitatively. The d -spacings of polyimides increase with the introduction of bridging groups, i.e., following the order: PDA < BZD < ODA < MDA < BDAF, while the densities increase in the order of MDA < BZD < PDA, and CEDs of polyimides change following the order of BDAF < MDA < ODA < BZD < PDA. For T_g prediction, no quantitative theory correlates the chemical structure and T_g . However, two important factors are well-known to influence T_g very much: the chain flexibility and the strength of interchain interaction. Furthermore, it is indicated that the strength of interchain interaction influences the T_g 's of polyimides much stronger than the chain flexibility. The T_g 's increase as the CEDs increase in the polyimides prepared from the same dianhydride and different diamines in this study.

References

1. Tang, Y. J.; Li, Y. S.; Ding, M. X. *Polym Bull* 1999, 42, 47.
2. Sykes, G. F.; Clair, A. K. S. *J Appl Polym Sci* 1986, 32, 3725.
3. Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers, Their Estimation and Correlation with Chemical Structure*; Elsevier: New York, 1976.
4. Lee, C. J. *J Macromol Sci Rev Macromol Chem Phys* 1989, 29, 431.
5. Liang, T. N.; Yang, X. Z.; Zhang, X. Y. *J Polym Sci Polym Phys* 2001, 39, 2243.
6. Damian, C.; Hurduc, N.; Hurduc, N.; Shanks, R.; Yarovsky, I.; Pavel, D. *Compos Mater Sci* 2003, 27, 393.
7. Bicerano, J. *Prediction of Polymer Properties*, 3rd ed.; Marcel Dekker: New York, 2002.
8. Mu, L. L.; Feng, C. J. *J Mol Sci* 2002, 18, 162.
9. Kier, L. B.; Hall, L. H. *Molecular Connectivity in Chemistry and Drug Research*; Academic Press: New York, 1976.
10. Kier, L. B.; Hall, L. H. *Molecular Connectivity in Structure-Activity Analysis*; Wiley: New York, 1986.
11. Hirayama, Y.; Yoshinaga, T.; Kusuki, Y.; Ninomiya, K.; Sakakibara, T.; Tamari, T. *J Membr Sci* 1996, 111, 169.
12. Tang, H.; Feng, H. Q.; Luo, H. B.; Dong, L. S.; Feng, Z. L. *Eur Polym J* 1997, 33, 519.