Structure and Properties of Aromatic 6-membered Polyimides Compared to 5-Membered Ones

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SUMMARY: When various properties of poly[2,5-di(n-alkyloxy)methyl-p-phenylenenaphthalene-1,8:4,5-diimide]s (Cm-NAPIs, m = 4, 6, 8) as aromatic 6-membered polyimides were compared with those of poly[2,5-di(n-alkyloxy)methyl-p-phenylenepyromellitimide]s (Cm-PYPIs, m = 4, 6, 8) as 5-membered ones, it was deduced that O atoms of C=O of Cm-NAPIs are not coplanar with their imide ring plane. This noncoplanarity led us necessarily to assuming that the 6-membered ring polyimide chains should have cis/trans-like isomeric structures. Detailed spectroscopic studies and ab initio calculations for appropriate model compounds are provided to support our assumption.

Introduction

Aromatic polyimides are the most important class of thermally stable polymers[1-3] currently used in many commercial applications. Of them poly(p-phenylenepyromellitimide)s are known to have the highest heat resistance[4]. This heat resistance results from their very high main chain rigidity and inter-chain attraction caused by the rigidity. However, chain rigidity is dependent not only on extent of electron delocalization along the main chain, but also on the resonance energy exerted by each group comprising the main chain. Therefore, it is readily expected that polyimide chains having larger fused aromatic rings are more rigid and heat-resistant than those having smaller fused aromatic rings, since the former possess higher hydrophobic interaction than the latter.

Out of these reasons we presumed that Cm-NAPIs having a four-fused ring system with a 6-membered imide ring should be more heat-resistant and crystalline than Cm-PYPIs having a three-fused ring system with a 5-membered imide ring. To study this problem we first prepared Cm-NAPIs and Cm-PYPIs. To the polymer backbones, we attached two (n-alkyloxy)methyl side branches to both the polyimides to enhance their solubilities[5-7], where n-alkyl groups were varied from n-butyl and n-hexyl to n-octyl. Chemical structures of these polymers are shown in Scheme 1.

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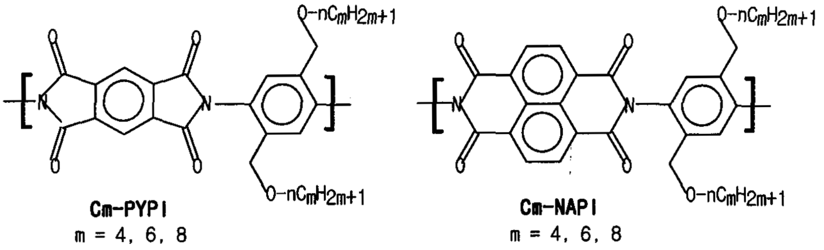


Cm-PYPI
m = 4, 6, 8

Cm-NAPI
m = 4, 6, 8

Scheme 1. Structure of the 5- and 6-membered polyimides

When physical and thermal properties of two polyimides were measured and compared to each other, we, contradictory to our expectation, found that Cm-NAPI chains are generally more flexible than Cm-PYPI chains, although a repeat unit of the former has one more ring than the latter. To elucidate this contradiction, we carried out detailed model studies by spectroscopic and ab initio-calculation methods and came to propose that the structure of a 6-membered imide ring is considerably different from that of a 5-membered one.

For these studies Cm-NAPIs and Cm-PYPIs had been prepared according to the method decribed in the literature[8,9)] and N,N'-diphenyl- and dibutylnaphthalene-1,8:4,5-diimide and N,N'-diphenyl- and dibutylpyromellitimide were prepared[10-12)] and used as model compounds. All the minimum energy structures and transition state structures were located with full geomety optimization by Hartree-Fock calculations using the 6-31G* basis set[13,14)].

Properties

Solubility. The purpose of appending side branches to main chain was to enhance solubility of the polymers, and solubilities of Cm-NAPIs and Cm-PYPIs were checked in various solvents. All the polymers were soluble in highly acidic solvents like H_2SO_4 or CH_3SO_3H. In polar aprotic solvents Cm-PYPIs did not show any solubility at all even on heating, while C8-NAPI was soluble in N,N-dimethylpropyleneurea(DMPU) and DMAc and C6-NAPI in DMPU at room temperature. This large solubility difference indicates that NAPIs have less strong inter-chain attraction than PYPIs.

Thermal properties. Thermal resistances measured by TGA at 20°C/min heating rate under N_2 were compared between the two kinds of polyimides and their TGA thermograms are reproduced in Fig. 1. As to see from it all the PYPIs, regardless of the

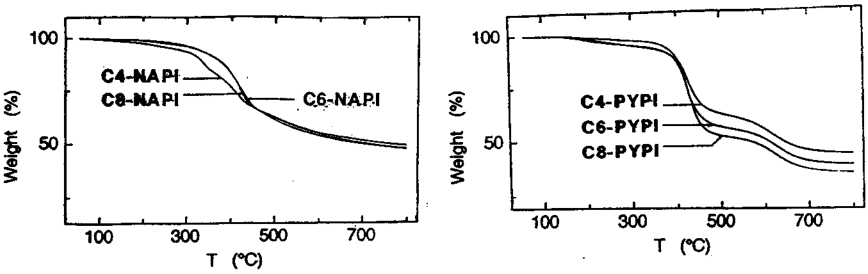


Fig. 1. TGA thermograms of Cm-NAPIs and Cm-PYPIs.

side chain length, revealed two-step pyrolysis behavior, in which side chain cleavage starts to take place at 395°C and main chain to break up at 575°C. But all the NAPIs gave smooth one-step pyrolysis behavior, in which side branches and main chain split away concurrently at 370°C. These experimental results indicate that at high temperatures there is eventually no interaction between side chain and main chain in Cm-PYPIs, while there is some in Cm-NAPIs. This means also that in interaction between main chains NAPIs are weaker than PYPIs. This weaker attraction must render NAPIs much less crystalline than PYPIs and even amorphous. The same result was really shown in WAXS study. All Cm-PYPIs are highly crystalline, while all Cm-NAPIs are completely amorphous.

UV-VIS spectra. UV-VIS spectroscopy is a powerful tool to obtain an information of extent of electron delocalization. Fig. 2 shows UV-VIS absorption behavior of the polyimides compared with the corresponding model compounds N,N'-diphenylnaphthalene-1,8:4,5-diimide(NAPI-M) and N,N'-diphenylpyromellitimide(PYPI-M). Fig. 2

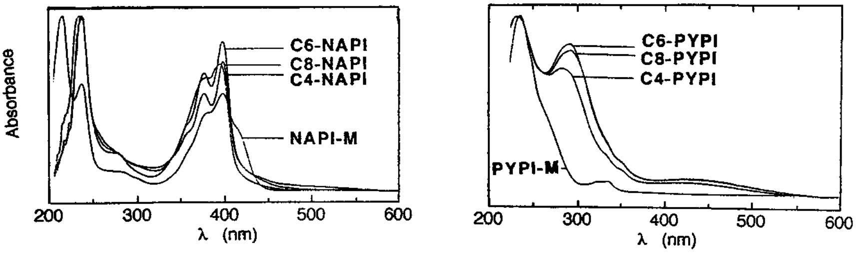


Fig. 2. UV-VIS spectra of polyimides and model compounds in H_2SO_4.

clearly shows that in the absorption maxima from both n-π* and π-π* transitions a bathochromic shift is observable between PYPIs and PYPI-M, indicating that π-electron conjugation length of PYPIs is longer than that of PYPI-M. However, between NAPIs and NAPI-M no such bathochromic shift can be observed, meaning that in NAPI main chains no π-electron delocalization is allowed. Later it was found that even the unpaired electrons on N atom can only poorly come into resonance with N-phenylene ring electrons, because N,N'-di(n-butyl)naphthaene-1,8:4,5-diimide revealed just the same UV-VIS spectrum as NAPI-M(Fig. 3). This difference in electron delocalizability along main chain between 5-membered imide ring and 6-membered one is the vital evidence of the difference in main chain rigidity between the two kinds of polyimides.

Ab initio calculation

To explain the reason why the π-electrons located on N-phenyl ring can be delocalized over 5-membered imide ring, while such delocalization is not allowed in 6-membered imide ring, ab initio calculations for N-phenylmaleimide and N-phenylnaphthalene-1,8-imide(Ph-NMI) were carried out by Hartree-Fock method using the 6-31G* basis set[13,14). From the calculations for N-phenylphthalimide were obtained: 1) The three bonds emanating from N atom are coplanar with sp^3 configuration, 2) the phenyl ring exists 53° tilted from the imide ring plane, and 3) the energy barrier for N-phenyl ring rotation is 14kJ/mol(3.3kcal/mol). These results indicate that in N-phenylphthalimide the π-electrons of phenyl ring can be slightly delocalized over 5-membered imide ring. From calculations for Ph-NMI were obtained: 1) The three bonds emanating from N-atom are also coplanar with sp^3 configuration, 2) the phenyl tilt angle is 90° and 2) the energy barrier for phenyl ring rotation is 68kJ/mol(16.2kcal/mol). These results indicate that the π-electrons existing at N-phenyl ring can not be delocalized over 6-membered imide ring at all.

Model studies

Model compounds. The ab initio calculation results can clearly explain that π-electron delocalizability makes Cm-PYPI main chains highly rigid, while the impossible π-electron delocalization renders Cm-NAPI main chains flexible. However, these results can not explain why Cm-NAPIs are amorphous and thermally less stable than Cm-PYPIs. To answer this question we conducted model studies. First we prepared N,N'-di(n-butyl)- and N,N'-diphenylpyromellitimide(C4-BDI) and Ph-BDI) and N,N'-di(n-butyl)- and N,N'-diphenylnaphthalene-1,8:4,5-diimide(C4-NDI and Ph-NDI) from routine condensation of n-butylamine and aniline with pyromellitic dianhydride and naphthalene-1,8:4,5-tetracarboxylic dianhydride, respectively.

UV-VIS spectra. For the model compounds we measured UV-VIS spectra again in concentrated H_2SO_4. These spectra are reproduced in Fig. 3. It clearly shows that Ph-BDI's maximum exists at lower wave length than C4-BDI, while Ph-NDI's spectrum is totally the same as C4-NDI's, although the N-substituent is changed from aromatic phenyl to aliphatic n-butyl. This result confirms again that no π-electrons located on the N-phenyl ring can come into conjugation over 6-membered imide ring, while it is allowed in 5-membered one.

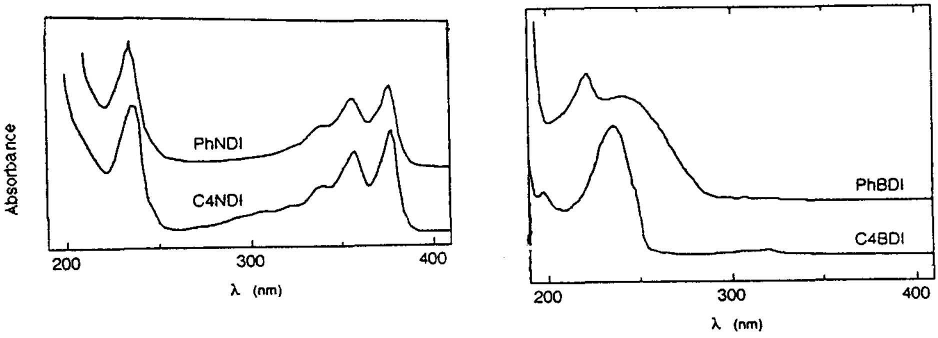


Fig. 3. UV-VIS spectra of the model compounds in H_2SO_4.

Solid-state ^{13}C-NMR spectra. The ab initio calculation has shown that the N-phenyl ring of N-phenylphthalimide is 53° tilted from 5-membered imide ring plane, while that of N-phenylnaphthalene-1,8-imide is 90° tilted from 6-membered imide ring plane. Based on this result it is reasonable to assume that two N-phenyl rings of Ph-BDI and Ph-NDI are also 53° and 90° tilted, respectively. If this assumption is true, we must naturally come to the deduction that in solid state the two N-phenyl rings of Ph-BDI must be in either parallel(53°/53°) or antiparallel(53°/147°) conformation and the two N-phenyl rings of Ph-NDI must have only one conformation(90°/90°). To confirm this deduction solid-state ^{13}C-NMR spectra of Ph-BDI and Ph-NDI were taken. Our interpretation of the ^{13}C-NMR spectrum of Ph-BDI could not find out any presence of two conformations, meaning that the above deduction is not true. However, in the spectrum of Ph-NDI a clear doublet of C=O carbon absorption was found, as to see from Fig. 4. This result means that in solid state Ph-BDI has only one conformation, while Ph-NDI has two conformations giving rise to two C=O carbons which are in different chemical environments.

To get more detailed understanding on the reason of C=O splitting into a doublet in Ph-

NDI, we also took a solid-state ^{13}C-NMR spectrum of C4-NDI. This spectrum exhibited only a singlet C=O carbon, meaning that the four C=O carbons of C4-NDI are chemically equivalent, and hence, C4-NDI has only one conformation in solid state. This spectral difference between C4-NDI and Ph-NDI results naturally from replacement of n-butyl group by phenyl group, meaning that the C=O absorption splitting of Ph-NDI arises from a certain influence of phenyl ring.

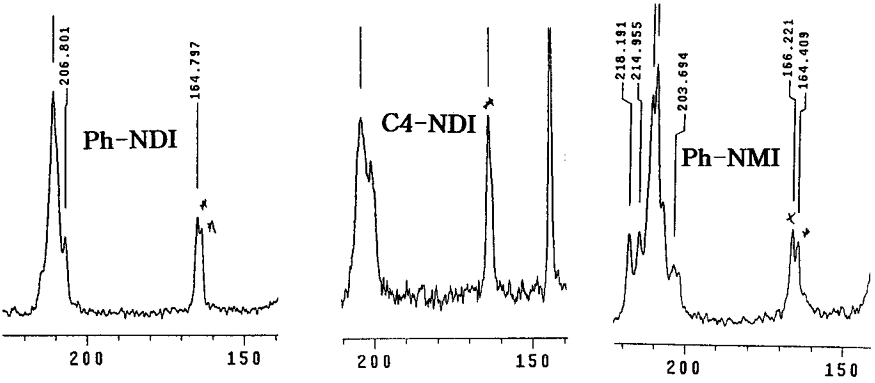


Fig. 4. MAS-^{13}C-NMR spectrum of Ph-NDI, C4-NDI and Ph-NMI.

To explain the presence of these two conformations, we made a simple molecular modeling calculation to obtain energy minimized configuration and torsional energy profile of N-phenylnaphthalene-1,8-imide(Ph-NMI) by CS Chem 3D program (Cambridge Scientific Computing, Inc.). The numerical torsional energy values obtained by rotating 180° around the N-C_{ph} were calibrated so that the maximum value corresponds to the value 16.2kcal/mol(68kJ/mol) obtained from the ab initio calculation, because absolute energy values calculated by simple simulation programs are not highly reliable$^{16)}$.

Torsional energy profile thus obtained is reproduced in Fig. 5. It shows that in the most stable state the N-phenyl ring is tilted about 45° from 6-membered imide ring plane. The destabilized state at 90° is the state formed by complete loss of resonance energy of 3.5kcal/mol. Fig. 5 shows further that there are two stable states, one at 45° and the other at 135°, but the 135°-state is a little bit more stable than the 45°-state. The result that even Ph-NMI which half-models the NAPI polymer has two different states must indicate that the two C=O groups contained in it must also be different from each other. This difference should be observable in ^{13}C-NMR spectroscopy. In Fig. 4 its solid-state

MAS-^{13}C-NMR spectrum is included. As it shows, this half-model compound has really two C=O peaks, which confirms the presence of two different C=O groups in it.

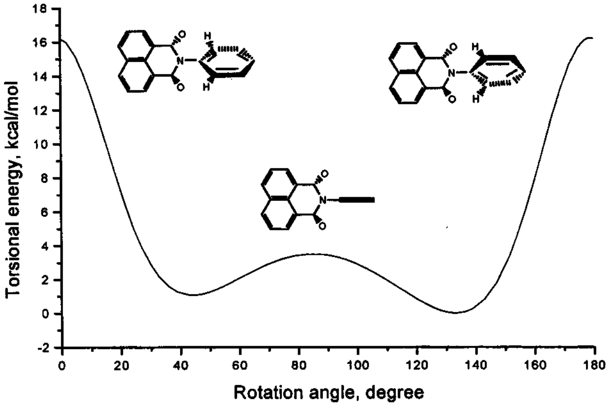


Fig. 5. Torsional energy profile of Ph-NMI around N-C$_{ph}$ bond

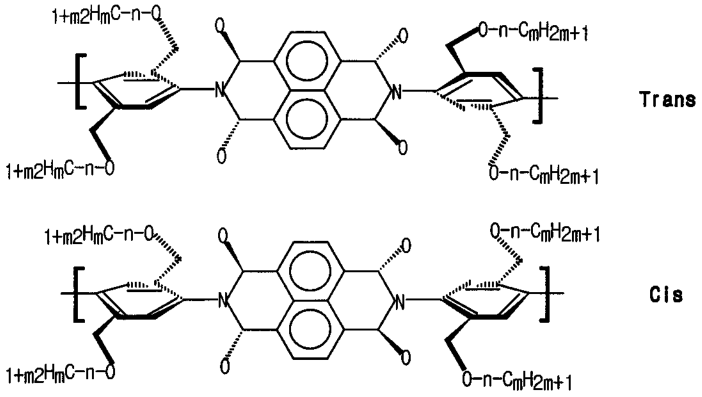
To explain these two different C=O groups, we assumed that the O atoms of C=O groups are not coplanar with the 6-membered imide ring plane, but a little bit distorted. When the imide plane is laid on paper plane, one O atom might direct downward and the other upward from paper plane. This distortion is caused by the hindered steric interaction between two H atoms at ortho position of N-phenyl ring and two O atoms bonded to C=O groups of 6-membered imide ring. This steric hindrance leads to a difficulty of free rotation of phenyl ring around N-C$_{Ph}$ bond, resulting to an atopoisomerism. This steric hindrance is not exerted in 5-membered imide ring, because the H-O distance is sufficiently long. This difference in rotation difficulty between 5- and 6-membered imide ring has already been evidenced by the result that torsional energy of 5-membered ring is only 3.3kcal/mol, while that of 6-membered one is 16.2kcal/mol. 3.3kcal/mol is certainly too small to observe in NMR.

Fig. 5 shows that Ph-NMI has resonance energy of 3.5kcal/mol. However, this value is apparently too small to observe in UV-VIS spectroscopy in solution, because in solution this small energy barrier can readily be overcome by rapid molecular movements.

As already described above, the 135°-state is a little bit more stable than the 45°-state. This stability difference can be readily understood when we consider the distance between $O_{C=O}$ and H atom at ortho position of phenyl($H_{O\text{-}Ph}$) in both the states. Two $H_{O\text{-}Ph}$

atoms come farther from $O_{C=O}$ in 135°-tilted state than in 45°-tilted state, as depicted in Fig. 5. Although this stability difference is quite small, and it can not be observable in solution. However, it is large enough to observe from solid-state ^{13}C-NMR spectroscopy of Ph-NMI, as shown in Fig. 4.

The fact that both Ph-NMI and Ph-NDI have a doublet C=O absorption in solid-state ^{13}NMR spectroscopy means that the C=O splitting of one 6-membered imide ring is not affected by the presence of the other one, although they are bound at the same molecule across the naphthalene ring. If it were affected, Ph-NDI should reveal more number of C=O peaks than a doublet.



Scheme 2. Proposed chain structure of Cm-NAPIs

When we now consider chain structure of NAPIs in solid state on the basis of our result of the isomeric structures of Ph-NMI and Ph-NDI, each N-phenylimide group can be in two states, regardless whether a naphthalene ring is substituted by one imide group or by two. This means that each NAPI repeat unit has two stable states in solid state. When these two states are depicted along the main chain of NAPI, there must be cis/trans-like structures, depending on orientation of C=O and phenyl groups. These cis and trans structures are depicted in Scheme 2. These cis/trans-like structures to be present in Cm-NAPIs can explain that they are amorphous in solid.

Conclusions

Unlike a 5-membered imide ring an N-aromatics-substituted 6-membered imide ring has two isomeric states in solid state, depending on orientation of C=O and N-aromatic group. This isomerism arises from the slightly hindered rotation of N-aromatic group. It leads to presence of cis/trans-like isomeric chain structures in 6-membered polyimides. The presence of these isomeric chain structures result to more flexible main chain nature, more amorphous morphology, lower thermal resistance and higher solubilities in organic solvents than the corresponding 5-membered polyimides.

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