

Synthesis and Characterization of fluorenyl Cardo Polyamide-imides

Zhiqiang Hu^{1,2} Shanjun Li^{1*} Chunhua Zhang² MingFan² Yinjie Chen

1. The Key Laboratory of Molecular Engineering of Polymer, Ministry of Education, and Department of Macromolecular Science, Fudan University, Shanghai, 200433, China
2. Shanghai Research Institute of Synthetic Resins, 200235, China

Abstract

A series of fluorenyl Cardo Polyamide-imides (PAIs) were synthesized by one-pot polycondensation of Cardo diamines, trimellitic anhydride and various aromatic diamines including p-phenylene diamine, m-phenylene diamine, 4,4'-oxydianiline, 3,4'-oxydianiline, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(3-amino phenoxy)phenyl]propane using triphenyl phosphite as condensing agents. Most of the polymers were readily soluble in aprotic polar solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), and *N,N*-dimethylformamide (DMF), as well as in less polar solvents such as dimethyl sulfoxide (DMSO), pyridine, and tetrahydrofuran etc. Polyamide-imides exhibited better solubility when alkyl substituents were incorporated. Inherent viscosities of these polyamide-imides in DMAc ranged from 0.44 to 0.88 dL/g. The glass transition temperatures of PAIs were in the range of 235–448°C by DSC and 5% weight loss temperature of all polymers exceed 400°C in air. The polymer films were flexible and had a tensile strength in the range of 64–111 MPa, an elongation at break in the range of 2.2–7.1%.

Keywords: Cardo; Fluorenyl polyamide-imide; solubility; properties

Introduction

Polyimides are well known as high performance polymers for their excellent heat resistance, electrical insulating properties, and mechanical characteristics, so they are widely used in fields of electrical materials, adhesives, and composite fiber and film materials [1-3]. However, they are generally insoluble and infusible in their fully imidized form, leading to processing difficulties; and this process of poly (amic acid) intermediate has several inherent problems such as emission of volatile byproducts (e.g., H₂O) and storage instability etc. The introduction of fluorenyl “cardo” groups into polymers such as polyimides[4-10], polyamides[11,12], polyquinolines[13] etc. can endow with them specific properties: (1)excellent heat resistance; (2)excellent solubility. Therefore, the introduction of “Cardo” groups into the backbone of polymers is an effective approach for improving solubility and thereby processability of polyimides. However, according to our previous study[14], the cardo polyimide contains a rigid bulky bis-phenylfluorene moiety and causes usually the film to be brittle.

Poly(amide-imide)s (PAIs), as a family, have deserved particular attention as they are probably the class of copolyimides that most closely resemble the thermal properties of aromatic polyimides. Furthermore, the inclusion of an amide group into the polyimide backbone increases its processability, solubility, and moldability, but thermal property was slightly decreased. Liaw and Yang [15-20] have done many eximious works about soluble polyamide-imides by the direct polycondensation of diimide-dicarboxylic acid and various in *N*-methyl-2-pyrrolidinone (NMP) using triphenyl phosphite as condensing agents.

In the present study, our objective is to investigate the effect of incorporation of alkyl

substituents in fluorenyl cardo diamines on the solubility and thermal stability of cardo polyamide-imides. Moreover, the effect of incorporation of amide-bond and the effect of linking structure of Cardo in polymeric backbone on the properties of PAIs were also discussed. A series of fluorenyl Cardo polyamide-imides were synthesized by one-pot polycondensation and characterized based on cardo diamines such as 9,9-bis(4-aminophenyl) fluorene(BAFL), 9,9-bis(3-methyl-4-aminophenyl)fluorene(BAFL(2Me)), trimellitic anhydride and various diamines such as p-phenylenediamine, m-phenylenediamine, 4,4'-oxydianiline, 3,4'-oxydianiline, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(3-aminophenoxy)phenyl]propane. The solubility, thermal properties and mechanical properties of the PAIs were investigated by TGA, DSC etc.

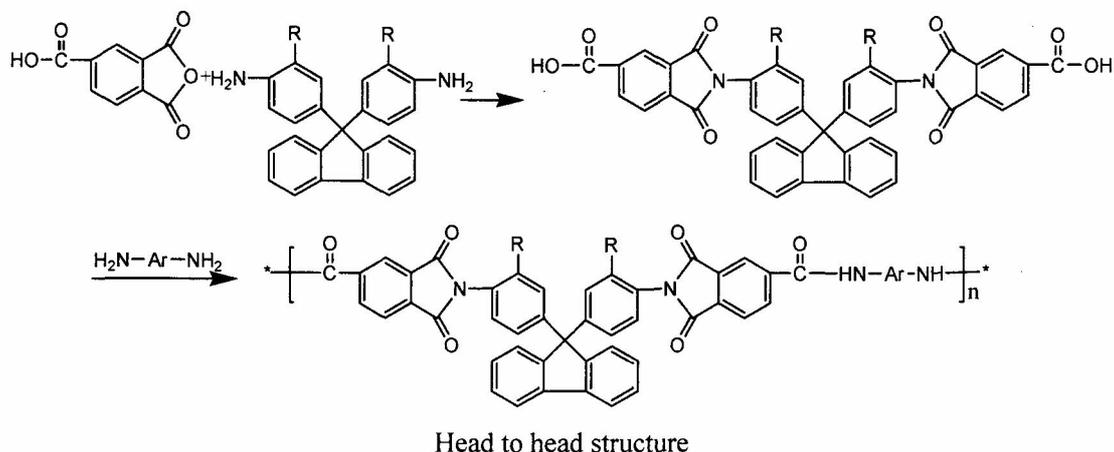
Experimental section

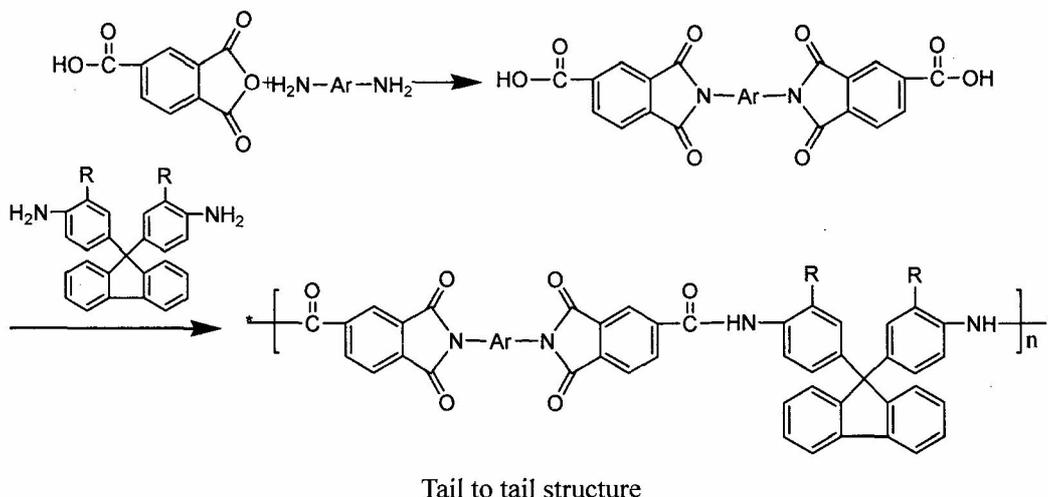
Reagents and Solvents

9,9-bis(4-aminophenyl)fluorene(BAFL), 9,9-bis(3-methyl-4-aminophenyl)fluorene(BAFL(2Me)), 3,4'-oxydianiline, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(3-aminophenoxy)phenyl]propane.(Shanghai Research Institute of Synthetic Resins), trimellitic anhydride (Lancaster), p-phenylenediamine, m-phenylenediamine, 4,4'-oxydianiline is the industry-class product. NMP and DMAc were dried in CaH_2 for 2 days and distilled before use.

Polyamide-imide synthesis

In a four-necked flask with a nitrogen inlet, a thermometer, a condenser and a mechanical stirrer, Cardo diamines and double molar trimellitic anhydride was dissolved in dried *N*-methyl-2-pyrrolidinone(NMP). The reactive mixture was refluxed under nitrogen atmosphere for a period of time, then equivalent molar diamine, and condensing agents including triphenyl phosphate, pyridine and CaCl_2 were directly added into the flask and constant stirring. The solution was stirred for about 3hr and a brown viscous solution was obtained. Then, the viscous solution was precipitated in methanol in a high speeding blender. The polyamide-imide powder was filtrated and washed by excess methanol and water, then was dried in a vacuum oven at 200°C for 12hr.





R=H(I), CH₃(II)

Ar=a-f

a	p-phenylenediamine (PDA)	
b	m-phenylenediamine (MDA)	
c	4,4'-oxydianiline (4,4'-ODA)	
d	3,4'-oxydianiline (3,4'-ODA)	
e	2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP)	
f	2,2-bis[4-(3-aminophenoxy)phenyl]propane (mBAPP)	

Fig. 1 Synthetic route of fluorenyl Cardo polyamide-imide

Preparation of Polyamide-imide Films

A solution was made by the dissolution of about 3 g of the polyamide-imide in 17mL of hot DMAc to afford an approximately 15 wt% solution. The clear solution was poured into 45cm×45cm plate glass which was placed in a 100 °C oven for 3 hr for evaporation of the solvent, then dried at 130°C for 2hr, 160°C for 2hr, 180 °C for 2hr, and 200°C for 2hr. The flexible PAI films with 50-60 μm thickness were then stripped from the glass substrate.

Measurements

IR spectra were recorded on a Nicolet 460. Inherent viscosity measurements were made with 0.5%(w/v)solution of polymers in DMAc at 25±0.1 °C using an Ubbelohde viscometer. The thermogravimetry analyses (TGA) were made with TA TGA Q50. Experiments were carried out under air and under N₂ atmosphere at a heating rate of 20 °C /min. Differential scanning

calorimetry (DSC) was carried out using TA DSC Q10 under N₂ atmosphere at a heating rate of 20 °C /min. Tensile properties were determined from stress-strain curves obtained with a LLOYD-LF according to GB13022.

Result and discussion

Synthesis of polyamide-imides

Polyamide-imides Ia-IIf were synthesized by one-pot direct polycondensation, not separating a diimide-dicarboxylic acid medium product, of Cardo diamines, trimellitic anhydride and various diamines in NMP using triphenyl phosphite as condensing agents. Intrinsic viscosity in DMAc of the polyamide-imides ranged from 0.44 to 0.88 dl/g. The structure of the PAIs was confirmed by IR. IR spectra of these PAIs revealed that the characteristic absorptions of imide groups appeared at 1780, 1720, and 1370cm⁻¹, and those of the amide group appeared around 3400 and 1670cm⁻¹.

Organo-solubility of polyamide-imides

As shown in Table 1, most of cardo polyimides being prepared from fluorenyl cardo diamines and other various aromatic diamines exhibited excellent solubility in common organic solvents such as, NMP, DMAc, DMF, DMSO, pyridine, and THF etc. It shows that the incorporation noncoplanar structure led by the introducing alkyl substituents on fluorenyl cardo diamine can significantly improve the solubility of cardo polyamide-imides in organic solvents. For example, BAFL(2Me)-4,4'-ODA and BAFL(2Me)-3,4'-ODA can partly dissolve in THF, but BAFL-4,4'-ODA and BAFL-3,4'-ODA is insoluble in THF, BAFL-BAPP and BAFL-mBAPP have a bad solubility in THF, but BAFL(2Me)-BAPP and BAFL(2Me)-mBAPP exhibit a excellent solubility in THF, it can be attributed to the incorporation of methyl substituent according to our previous study[14]. Meanwhile, it was found that the solubility of cardo polyamide-imides increases with increasing of the distance among the imide-rings, isomer of aromatic diamine also improve its solubility in organic solvents.

Table 1 Organo-solubility^a and Inherent viscosity^b of polyamide-imides

Code	Polymer	NMP	DMAc	DMF	Py	THF	DMSO	η (dl/g)
Ia	BAFL-PDA	S	S	S	S	Ins	S	0.85
aI	PDA-BAFL	S	S	S	S	Ins	S	0.69
Ib	BAFL-MDA	S	S	S	S	Ins	S	0.63
bI	MDA-BAFL	S	S	S	S	Ins	S	0.55
Ic	BAFL-4,4'-ODA	S	S	S	S	Ins	S	0.88
cI	4,4'-ODA-BAFL	S	S	S	S	Ins	S	0.79
Id	BAFL-3,4'-ODA	S	S	S	S	SW	S	0.67
dI	3,4'-ODA-BAFL	S	S	S	S	SW	S	0.62
Ie	BAFL-BAPP	S	S	S	S	PS	S	0.62
eI	BAPP-BAFL	S	S	S	S	SW	S	0.72
If	BAFL-mBAPP	S	S	S	S	SW	S	0.55
fI	mBAPP-BAFL	S	S	S	S	S	S	0.44

Ila	BAFL(2Me)-PDA	S	S	S	S	SW	S	0.54
Ilb	BAFL(2Me)-MDA	S	S	S	S	PS	S	0.56
Ilc	BAFL(2Me)-4,4'-ODA	S	S	S	S	PS	S	0.73
Ild	BAFL(2Me)-3,4'-ODA	S	S	S	S	PS	S	0.52
Ile	BAFL(2Me)-BAPP	S	S	S	S	S	S	0.57
IIf	BAFL(2Me)-mBAPP	S	S	S	S	S	S	0.64

a. S: Soluble, PS: Part soluble, SW: Swelling, Ins: insoluble

b. Intrinsic viscosities measured in DMAc at 25°C

Tg and thermal stability of PAIs

The Tg value of Cardo polyamide-imides measured by using TA DSC Q10 differential scanning calorimetry (DSC) using under N₂ atmosphere at a heating rate of 20°C/min. Tg of the polyamide-imides increase with rigid increase of other diamines (BAFL-PDA (448°C) > BAFL-MDA (412°C) > BAFL-4,4'-ODA (374°C) > BAFL-BAPP (318°C) > BAFL-3,4'-ODA (292°C) > BAFL-mBAPP(244°C) and PDA-BAFL (414°C) > MDA-BAFL (384°C) > 4,4'-ODA-BAFL (371°C) > BAPP-BAFL (320°C) > 3,4'-ODA-BAFL (300°C) > mBAPP-BAFL(235°C)) whether head to head structure or tail to tail structure. Tg of PAIs containing head to head structure is higher than those containing tail to tail structure when diamine is very rigid PDA or MDA, but the difference isn't obvious with the flexible increase of diamines. In addition, as shown in Table 2, all polyamide-imides with para position structure have higher Tg than these with meta position structure.

Moreover, to discuss thermal and thermal stability, the onset temperature corresponding to 5%, 10% and 15% weight loss of this system was measured by TGA under air and under nitrogen respectively (Table 2). All polyimides show good thermal stability, powder samples of these polyimides undergo 5% weight loss in the range of 405°C -502°C in air at a heating rate of 20°C/min and char yields of 54%-64% at 800°C. under nitrogen atmosphere. PAIs containing head to head structure behaves relatively better thermal stability than those containing tail to tail linking structure of Cardo in polyamide-imides backbone.

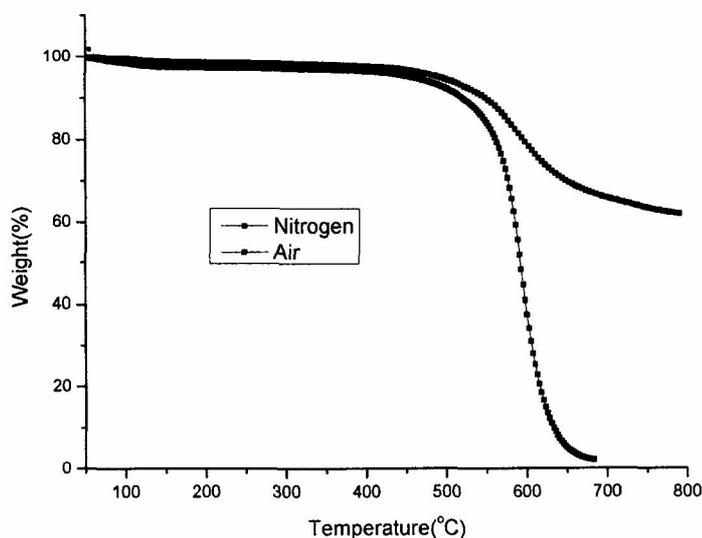


Fig. 2 TGA curves of polymer Ic under Air and nitrogen atmosphere

Table 2 Tg and thermal stability of PAIs

Code	Polymer	T _{max} (°C)		TGA Weight loss(°C)						Tg (°C)	Yc(%)
				5%		10%		15%			
		Air	N ₂	Air	N ₂	Air	N ₂	Air	N ₂		
Ia	BAFL-PDA	593	587	478	480	535	545	558	574	448	64.
aI	PDA-BAFL	593	599	426	449	515	528	544	563	414	59
Ib	BAFL-MDA	592	591	439	471	531	549	555	577	412	63
bI	MDA-BAFL	589	477, 596	454	460	527	531	556	567	384	61
Ic	BAFL-4,4'-ODA	593	592	405	491	510	548	542	575	374	61
cI	4,4'-ODA-BAFL	598	601	478	476	530	545	555	575	371	61
I d	BAFL-3,4'-ODA	597	593	502	495	545	555	563	581	292	63
dI	3,4'-ODA-BAFL	595	467, 617	451	457	524	540	554	585	300	61
Ie	BAFL-BAPP	591, 639	544, 585	474	478	522	522	551	548	318	62
eI	BAPP-BAFL	479, 593	535, 587	454	450	499	485	541	519	320	59
If	BAFL-mBAPP	598, 649	545, 584	479	469	531	521	561	550	244	63
fI	mBAPP-BAFL	470, 585	532, 585	459	483	495	512	531	528	235	55
I Ia	BAFL(2Me)-PDA	546,571	576	463	490	493	523	514	546	—	56
I Ib	BAFL(2Me)-MDA	574	540,577	459	485	496	515	517	535	379	55
I Ic	BAFL(2Me)-4,4'-ODA	573	579	454	485	483	533	509	569	382	63
I Id	BAFL(2Me)-3,4'-ODA	548	526	450	482	480	508	505	525	330	54
I Ie	BAFL(2Me)-BAPP	453,574	516	440	470	467	504	493	535	335	59
I If	BAFL(2Me)-mBAPP	420, 569	524	443	482	474	507	501	524	299	56

T_{max}= The maximum decomposition temperature;

Yc=The char yield at 800 °C.

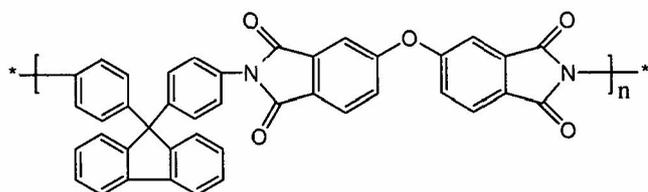
Mechanical Properties of PAIs Film

Mechanical properties of the PAIs films were measured, the results of tensile strength, elongation at break, and tensile modulus are summarized in Table 3. The polymer films had tensile strength of 64-111MPa, Elongation to Break of 2.2-7.1%, tensile modulus about 3.0GPa, indicating that they are strong and hard materials. According our previous study, mechanical properties of the film obtained by casting the solution of polyimide(BAFL-ODPA) could not be measured, thus, it indicates that the incorporation of an amide group into the polyimide backbone improve its mechanical properties, and thermal stability of these polymers is still excellent.

Table 3 Mechanical properties of the PAIs films

Code	Polymer	Tensile Strength MPa	Elongation to Break in %	Tensile modulus Gpa	Film Quality
Ia	BAFL-PDA	92	3.2	—	Flexible
aI	PDA-BAFL	81	2.7	—	Flexible
Ib	BAFL-MDA	99	4.4	—	Flexible
bI	MDA-BAFL	66	2.0	—	Flexible
0Ic	BAFL-4,4'-ODA	90	7.1	—	Flexible
cI	4,4'-ODA-BAFL	91	3.9	—	Flexible
I d	BAFL-3,4'-ODA	71	4.7	—	Flexible
dI	3,4'-ODA-BAFL	83	4.4	—	Flexible
Ie	BAFL-BAPP	97	7.1	—	Flexible
eI	BAPP-BAFL	71	7.0	—	Flexible
If	BAFL-mBAPP	64	3.0	—	Flexible
fI	mBAPP-BAFL	84	4.1	2.8	Flexible
IIa	BAFL(2Me)-PDA	107	2.2	3.5	Flexible
IIb	BAFL(2Me)-MDA	67	2.9	2.9	Flexible
IIc	BAFL(2Me)-4,4'-ODA	111	4.3	—	Flexible
IId	BAFL(2Me)-3,4'-ODA	108	4.6	—	Flexible
IIe	BAFL(2Me)-BAPP	107	4.4	3.3	Flexible
II f	BAFL(2Me)-mBAPP	81	3.6	3.2	Flexible
Ref	BAFL-ODPA	—	—	—	Brittle

Ref:



Conclusion

A series of polyamide-imides by one-pot direct polycondensation were synthesized, and the effect of incorporation of alkyl substituents in fluorenyl cardo diamines and aromatic diamine on the solubility and thermal stability of cardo polyamide-imides were investigated. Moreover, the effect of incorporation of amide-bond and the effect of linking structure of Cardo in polymeric backbone on the properties of PAIs were also discussed. Most of the polymers were readily soluble in aprotic polar solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), and *N,N*-dimethylformamide (DMF), as well as in less polar solvents such as dimethyl sulfoxide (DMSO), pyridine, and tetrahydrofuran etc, and polyamide-imides exhibited better solubility when alkyl substituents were incorporated. Inherent viscosities of these polyamide-imides in DMAc ranged from 0.44 to 0.88 dL/g. The glass transition temperatures of PAIs were in the range of 235–448°C by DSC and 5% weight loss temperature of all polymers exceed 400°C in air. The polymer films had a tensile strength in the range of 64–111 MPa, an elongation at break in the range of 2.2–7.1%.

References

1. Mittal, K.L.(Ed.)Polyimides: Synthesis, Characterization, and Application, Vols. 1 and 2; Plenum: New York, 1984.
2. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M.(Eds.)Polyimides; Blackie & Son: Glasgow, UK, 1990.
3. C.P. Yang, J.A.Chen, J Polym Sci, Polym Chem, 1999; 37:1681-1691.
4. Korshak VV, Vinogradova SV, Vygodski YS. J Macromol Sci Rev Macromol Chem 1974; C11:45.
5. Reddy TA, Srinivasan M. J Polym Sci: Part A: Polymer Chemistry, 1989; 27:1419-1427.
6. Hsiao SH, Li CT. J Polym Sci: Part A: Polymer Chemistry, 1999; 37:1403-1412.
7. Michinori Nishikawa Poly. Adv. Technol. 2000; 11:404-412.
8. Nathakie Biolley, martine Gregoire, Thierry Pascal, Bernard Sillion Polymer 1991; 32:3256-3261.
9. E. Said-Galauiev, Ya.Vygodskii etc. J. of Supercritical Fluids 2003;27: 121-130.
10. L. Dutruch, T. Pascal etc. Poly. Adv. Technol. 1996; 8:8-16.
11. A.D.Sagar, R.D.Shingte, P.P.Wadgaonkar, M.M.Salunkhe. European Polymer Journal 2001; 37:1493-1498.
12. P.R.Srinivasan,V.Mahadevan, M.Srinivasan. Journal of Polymer Science: Part A: Polymer Chemistry edition, 1989;19: 2275-2285.
13. Stille JK, Harris RM, Padaki SM. Macromolecules 1981; 14:486-493.
14. Zhiqiang-Hu, Minghai-Wang, Shanjun-Li, xiaoyun liu etc., Polymer 2005; 46:5278-5283.
15. D.J. Liaw, B.Y. Liaw, C.W. Yu, J Polym Sci, Polym Chem, 2000; 38:2787-2793.
16. D.J. Liaw, B.Y. Liaw, E.T. Kang, Macromol. Chem. Phys. , 1999; 200:2402-2406.
17. D.J. Liaw, P.N.HSu, W.H.Chen, B.Y.Liaw, J Polym Sci, Polym Chem, 2001; 39:3498-3504.
18. S.H. Hsiao, C.P. Yang, J Polym Sci, Polym Chem, 1991; 29:447-452.
19. C.P. Yang, C.C. Yang, R.S. Chen, J Polym Sci, Polym Chem, 2001; 39:2591-2601.
20. C.P. Yang, J.M. Cheng, S.H. Hsiao, Die Makromolekulare Chemie, 1992; 193:445-453.