

Synthesis and Characterization of 4,5-Bis(4-fluorobenzoyl)-1-Methylcyclohexene and Its Polyethers

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ABSTRACT: A new difluoride 4,5-bis(4-fluorobenzoyl)-1-methylcyclohexene (DFKK) has been prepared with fumaryl chloride, fluorobenzene, and 2-methyl-1,3-butadiene as starting materials through two steps of reactions. This DFKK monomer undergoes reaction with 2,2-(*p*-hydroxyphenyl)-*iso*-propane (BPA) in the presence of excess anhydrous potassium carbonate in sulfolane to give a high molecular weight reactive poly(ether ketone ketone) (PEKK) that is very soluble in solvents such as chloroform and *N,N*-dimethylformamide at room temperature, has glass transition temperature of 182°C, and is easily cast into flexible and bale ivory film with tensile strength of 64 MPa. The 5% weight loss temperature is 407°C. Ring-closing reaction of PEKK with hydrazine gives cyclized PEKK (CPEKK) with improved thermal stability and reduced solubility. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1866–1871, 2002; DOI 10.1002/app.10454

Key words: 4,5-bis(4-fluorobenzoyl)-1-methylcyclohexene; reactive; poly(aryl ether ketone); ring-closing reaction

INTRODUCTION

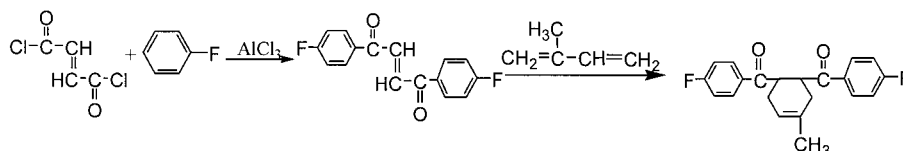
Poly(aryl ether ketone)s (PAEK) comprise a class of polymers exhibiting high thermal stability and excellent electric and mechanical properties.^{1–7} For the highest performance applications, poly(ether ether ketone) (Vetrix PEEK), which was developed by the ICI Company, has proved very effective and has been successfully commercialized.⁸ This material is widely used as an insulating material and as high-temperature matrix resin for composites. However, most of the poly(aryl ether ketone)s including Vetrix PEEK are highly crystalline and very insoluble in all common solvents at ambient temperatures. To avoid precipitation of low molecular crystalline from solution, synthesis reaction conditions for obtaining high molecular weight polymers have to be

rigorous. For example, the synthesis of Vetrix PEEK is generally performed at 300°C in diphenylsulfone. The purification of the polymer, in particular the removal of the inorganic salt, is rather difficult because of the insolubility too. For these reasons, the main interest in the PAEK family of engineering thermoplastics has been directed toward synthesizing soluble, amorphous PAEKs with high glass transition temperatures under mild reaction conditions. In the past decade, many amorphous PAEKs have been synthesized via nucleophilic displacement reaction by using bisphenols or dihalides that will incorporate asymmetric moieties or bulky groups into the polymer backbone or as pendant groups on the polymer molecular chain.^{9–15}

In the realm of high performance polymer materials, there is a never-ending search for a wider application. For PAEK, much attention is paid to reactive or functional poly(aryl ether ketone)s in recent years.^{16–18} The functionalization of PAEK can be achieved either by chemical modification of

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Scheme 1

polymers or by synthesis of functional monomers. We describe here the synthesis of asymmetric functional 4,5-bis(4-fluorobenzoyl)-1-methylcyclohexene as a new difluoride monomer and the preparation of soluble and reactive poly(ether ketone ketone) by the nucleophilic displacement polymerization of this difluoride with 2,2-(*p*-hydroxyphenyl)-*iso*-propane (BPA). This soluble reactive polymer containing asymmetric moieties and double bonds along the polymer chain is further converted into cyclized PEKK (CPEKK) via ring-closing reaction with hydrazine.

EXPERIMENTAL

Materials

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. Fluorobenzene was dried with CaCl_2 before usage. Sulfolane was distilled before the reaction.

1,2-Bis(4-fluorobenzoyl)ethylene

To a solution of 86.8 g (0.651 mmol) aluminum chloride in 500 mL carbon disulfide was added 50 g (0.52 mol) fluorobenzene. The resulting suspension was gently refluxed under a nitrogen atmosphere. The amount of 28.2 mL (0.26 mmol) fumaryl chloride was added over a period of 20 min. The resulting dark orange reaction mixture was refluxed for 18 h, and the residue was poured onto 1 kg of crushed ice and 15.0 mL concentrated hydrochloric acid. The semisolid was filtered off, washed with ethanol, and recrystallized from toluene to give pale yellow needles in 96% yield: mp 115°C, $^1\text{H-NMR}$ δ 7.18 (t, 4H, 2 *ortho* $\text{C}_6\text{H}_2\text{F}$), 7.97 (s, 2H, CH=CH), 8.08 (d, 4H, 2 *ortho* $\text{C}_6\text{H}_2\text{CO}$).

4,5-Bis(4-fluorobenzoyl)-1-Methyl-Cyclohexene

To a solution of 136 g (0.5 mol) 1,2-bis(4-fluorobenzoyl)ethylene in 400 mL benzene was added 177 g (2.6 mol) 2-methyl-1,3-butadiene. Then the reaction mixture was heated at 80°C until a col-

orless reaction mixture resulted. The reaction mixture was filtered at room temperature, and the resulting residue was recrystallized from *n*-butanol to give a white crystalline in 100% yield: mp 115–116°C, $^1\text{H NMR}$ δ 1.71 (s, 3H, CH_3), 1.95–2.58 (m, 4H, CH_2), 4.10 (m, 2H CH—CH), 5.50 (t, 1H, CH=C), 7.15 (m, 4H, 2 *ortho*, $\text{C}_6\text{H}_2\text{F}$), 8.08 (m, 4H, 2 *ortho* $\text{C}_6\text{H}_2\text{CO}$), infrared (IR) part absorption bands 1680 cm^{-1} (C=O), 1600 cm^{-1} , 1500 cm^{-1} , 1414 cm^{-1} and 850 cm^{-1} (C=C and phenyl), 1230 cm^{-1} (C-F).

Poly(ether ketone ketone)

A three-necked flask that was equipped with a nitrogen inlet, thermometer, Dean-Stark trap, and condenser was charged with 3.442 g (0.015 mol) BPA, 5.109 g (0.015 mol) DFKK and 2.902 g (0.021 mol) K_2CO_3 . The amount of 34.5 mL of sulfolane and 34.5 mL of chlorobenzene were added under the protection of nitrogen. The reaction mixture was heated to about 150°C. Upon dehydration and removal of chlorobenzene, the reaction temperature gradually increased to 200°C. When the solution viscosity did not increase obviously, 20 mL of chloroform was added to dilute the solution. Then, the polymer solution was filtered to remove salt, coagulated in 50 mL of ethanol and filtered, redissolved in chloroform, filtered, and coagulated in ethanol. The white fibrous polymer was cooked in water for three times and dried in a vacuum oven at 100°C for 24 h to give PEKK.

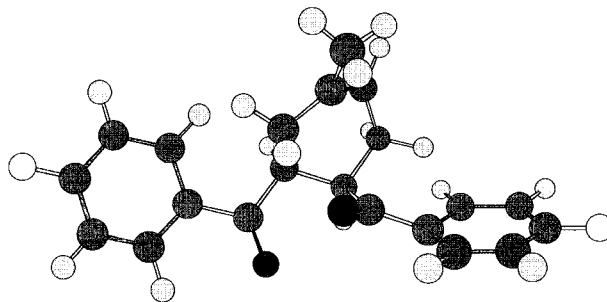
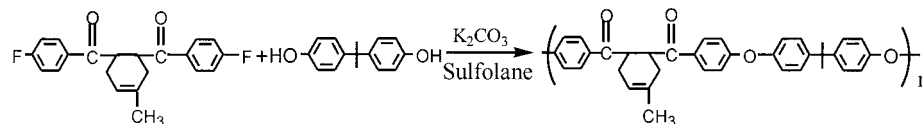


Figure 1 Suggested model of DFKK generated by Chem 3 molecular modeling program.



Scheme 2

Ring-closing reaction

A three-necked flask that was equipped with a thermometer, condenser, and mechanical stirrer was charged with 3 g PEKK, 20 mL of sulfolane, and 10 mL of chlorobenzene. The resulting mixture was heated to and maintained at 100°C. Ten milliliters of 50% hydrazine in water was added dropwise, followed by refluxed for 8 h. Chlorobenzene was then removed under reduced pressure. The polymer solution was coagulated in water and filtered, cooked in water, and filtered for three times. The obtained polymer was dried in a vacuum oven at 100°C for 24 h to give CPEKK.

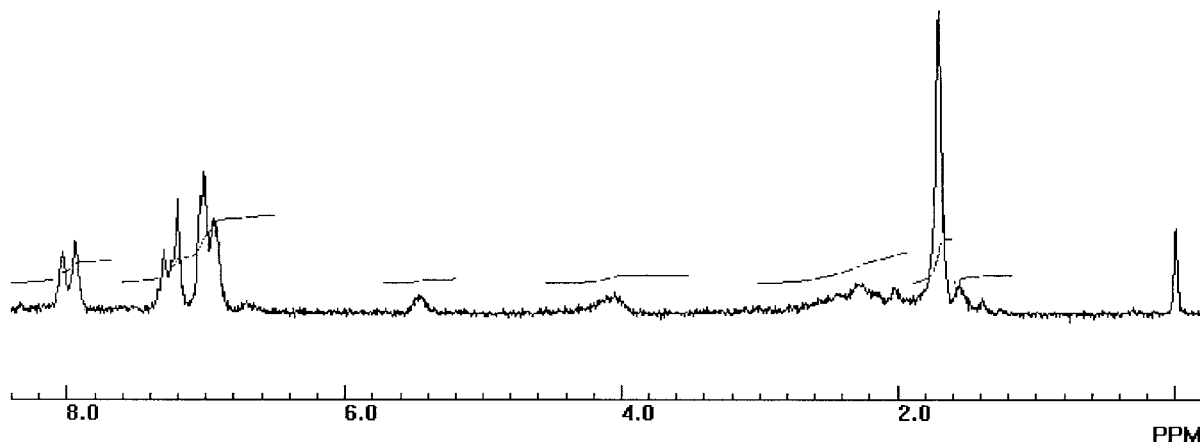
Characterization

¹H-NMR spectra were recorded on a JEOL FX-90Q instrument using tetramethylsilane as the internal standard, and deuteriodimethylsulfoxide or deuteriochloroform as solvent. IR spectra were recorded on a Nicolet-5DX Fourier transform infrared spectrometer. Inherent viscosity measurements were performed in CHCl₃ at 25°C by using a Ubbelohde dilution viscometer. Glass transition temperatures were measured on a Dupont 200 DSC instrument at a heating rate of 10°C/min. Thermogravimetric analysis was made on a Perkin-Elmer TGA module (in an air atmosphere) with a heating rate of 10°C/min. Tensile test was

performed on a Shimadzu tensile tester (model AG-2000) at a strain rate of 10 mm/min.

RESULTS AND DISCUSSION

1,2-Bis(4-fluorobenzoyl)ethylene (BFBE) was prepared according to the method described by Adams and Hay.^{19,20} Fluorobenzene and fumaryl chloride were reacted in a Friedel-Crafts reaction to give BFBE.¹⁹ A Diels-Alder reaction of BFBE with 2-methyl-1,3-butadiene gave in excellent yield 4,5-bis(4-fluorobenzoyl)-1-methylcyclohexene (DFKK) (Scheme I). The structures of DFKK and intermediate BFBE were found by IR and ¹H NMR spectroscopy. As shown in experimental, the signals of H atoms in ¹H-NMR and absorption bands in IR could be easily assigned. The suggested model of DFKK generated with the help of Chem 3D molecular modeling program is shown in Figure 1. Compared with 4,5-bis(4-fluorobenzoyl)-cyclohexene, which was previously prepared by Hay²⁰ from the reaction of BFBE with 1,3-butadiene, DFKK is more asymmetric and twisty, polymers containing these moieties in the polymer backbone would not be expected to crystallize and would be expected therefore to be soluble and remain in solution during polymerization.

Figure 2 ¹H NMR spectrum of PEKK.

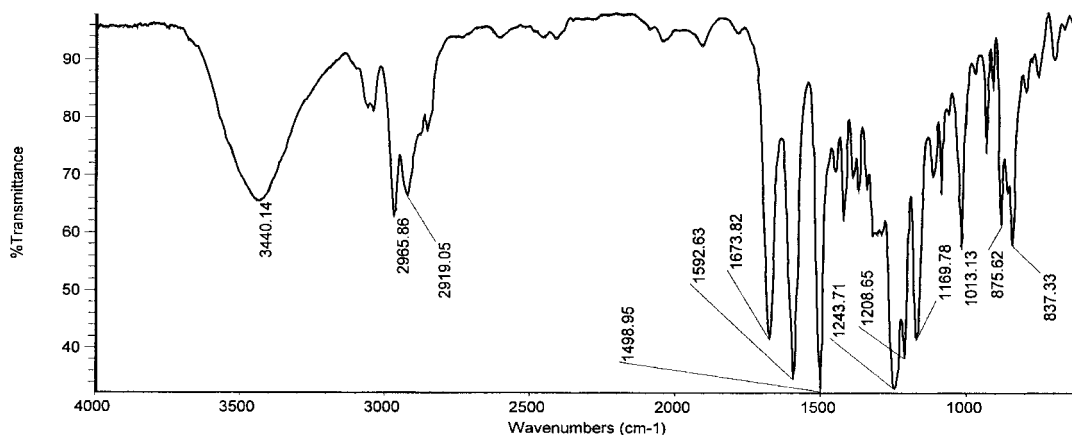
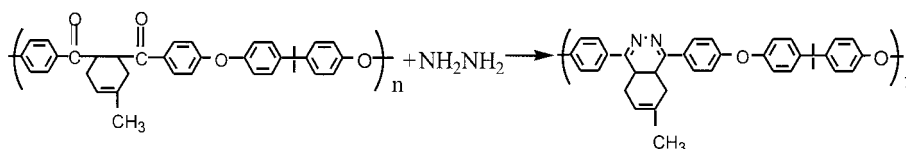


Figure 3 IR spectrum of PEKK.



Scheme 3

In the nucleophilic displacement polymerization reaction, which is illustrated in Scheme II, the solid composition, weight percent of DFKK, BPA, and K_2CO_3 , was maintained at 25 wt %, and any water present or generated during the bisphenoxide formation was removed as an azeotrope with chlorobenzene. The reaction was gradually heated to $150^\circ C$. Upon completion of bisphenoxide formation and dehydration, it was heated to and maintained at $200^\circ C$ to effect the displacement reaction. After a period of 8 h, the inherent viscosity of PEKK measured in chloroform at

$25^\circ C$ was 1.26 dL/g. 1H NMR and IR were used to determine the structure of PEKK. In the 1H -NMR spectrum (Fig. 2), signals for the protons of PEKK are identical as follows: δ 1.71 (s, 9H, CH_3), 2.14–2.34 (m, 4H, CH_2), 4.05 (m, 2H, $CH-CH$), 5.36–5.56 (m, 1H, $CH=C$), 6.92–7.31 [m, 12H, 2 *ortho* C_6H_2O and 2 *ortho* $C_6H_2C(CH_3)_2$], 7.94–8.03 (m, 4H, 2 *ortho* C_6H_2CO). In the IR spectrum (Fig. 3), part absorption bands are identical as follows: 1674 cm^{-1} ($C=O$); 1593 cm^{-1} , 1499 cm^{-1} , and 837 cm^{-1} ($C=C$ and phenyl); 2966 cm^{-1} and 2919 cm^{-1} (CH_3 and CH_2). The double bond in the

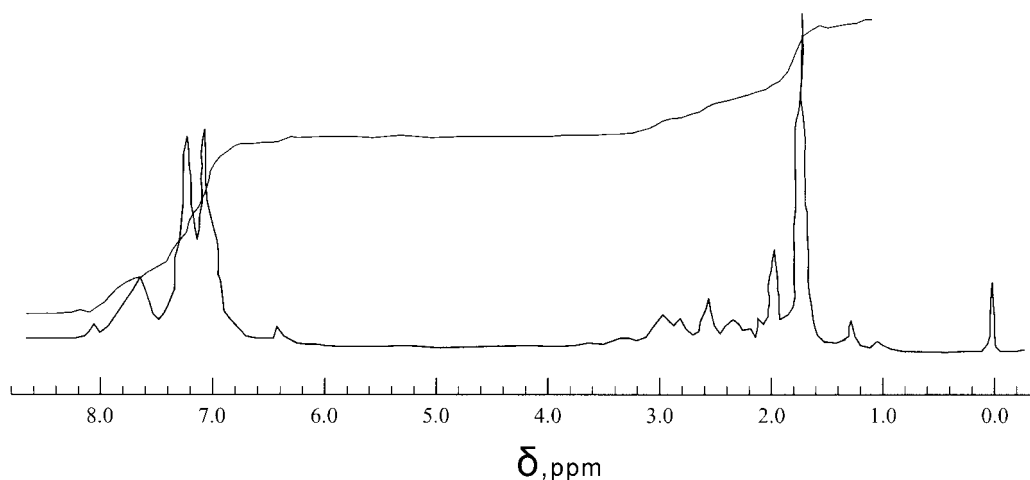


Figure 4 1H NMR spectrum of CPEKK.

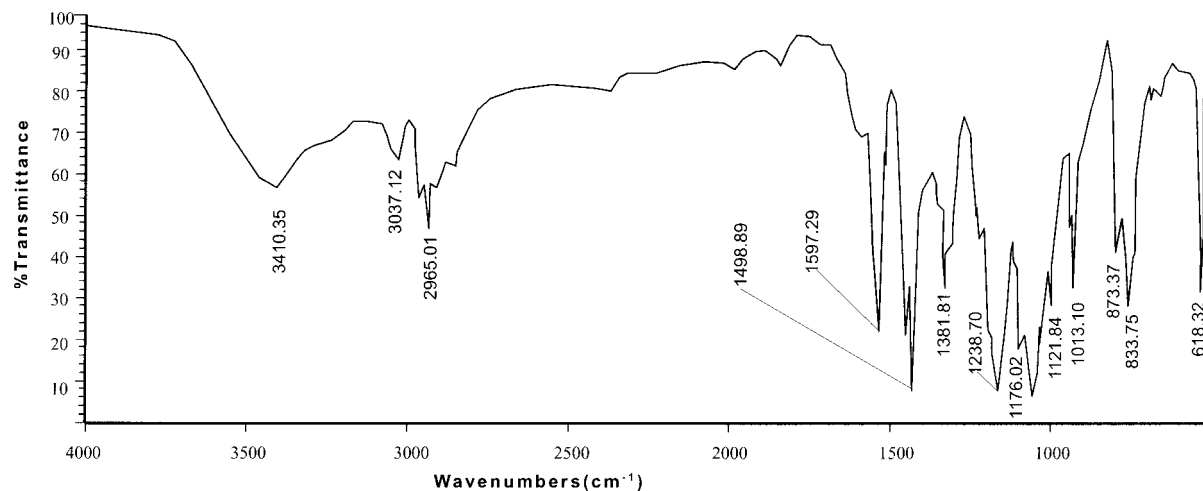


Figure 5 IR spectrum of CPEKK.

cyclohexene structure makes PEKK different from other PAEKs. Because double bonds in the polymer chains could be converted into other functional groups such as carboxyl, aminoaniline, halide, and sulfonic acid, the PEKK is reactive. As a result, PEKK derivatives could be used in more fields such as polymer reagent, polymer support, and polymer catalyst. The PEKK could be solution cast from chloroform at room temperature to give flexible, clear, and pale ivory film. This film has tensile strength of 64 MPa, elongation at break of 6.4%, and initial modul of 0.92 GPa. The film behaves as tough material and high initial modulus. In addition, as expected, PEKK is easily soluble in many organic solvents such as chloroform, chlorobenzene, sulfolane and DMAc.

Carbonyl groups on *ortho* positions of cyclohexene moieties along the polymer main chain make

it possible for PEEK to be cyclized with hydrazine (Scheme III). The cyclization reaction was conducted in a sulfolane/chlorobenzene (2/1) solvent mixture at 100°C. Hydrazine was added dropwise. To acquire completely cyclization, the reaction was conducted for a long period of time (8 h). Obtained polymer, CPEKK, was characterized with ^1H NMR (Fig. 4) and IR (Fig. 5). Comparing Figure 3 with Figure 5, it can be seen that the absorption band of $\text{C}=\text{O}$ at 1674 cm^{-1} in the IR spectrum of PEKK disappears in the IR spectrum of CPEKK after cyclization. Comparison of Figure 2 with Figure 4 also shows that the surroundings of H atoms in polymer chain have changed after cyclization. Disappearance of strong electron-drawing carbonyl makes chemical shifts of H atoms near them move to higher magnetic domain in ^1H -NMR spectrum. Cyclization of PEKK with hydrazine also brings changes in properties of polymer. Solubility and thermal properties of PEKK and CPEKK are listed in Tables I and II, respectively. Thermal behavior of the polymers was evaluated with DSC and thermogravimetric

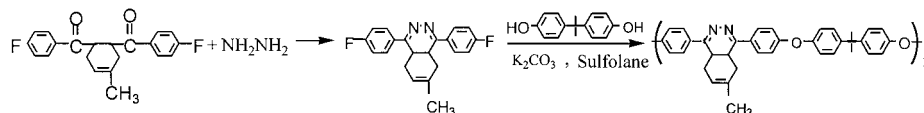
Table 1 Solubility of PEKK and CPEKK^a

Solvent	Polymer	
	PEKK	CPEKK
<i>N,N</i> -Dimethylacetamide	+	±
Chloroform	+	±
<i>N,N</i> -Dimethylformamide	+	±
Dimethylsulfoxide	-	-
<i>N</i> -Methyl-2-pyrrolidone	+	+
Tetrachloroethane	+	+
Tetrahydrofuran	+	+
<i>o</i> -Dichlorobenzene	+	±
Pyridine	+	+

^a+, Fully soluble; ±, partially soluble; -, insoluble.

Table II Thermal Properties of PEKK and CPEKK

Polymer	Property	
	T_g (°C)	5% Weight Loss Temperature (°C)
PEKK	212	407
CPEKK	242	407
Difference	30	Very small



Scheme 4

analysis (TGA). Table I shows that the glass transition temperature (T_g) of CPEKK is 30°C higher than that of PEKK. The higher T_g observed in CPEKK is attributed to the more rigid backbone of CPEKK, resulting from a change of rotating carbonyl groups into pyrazine moieties. However, the decomposition temperature at which 5% weight loss of CPEKK in air took place does not change obviously. For both PEKK and CPEKK, decomposition of C(CH₃)₂ groups, first taking place at elevated temperature may explain this phenomenon. CPEKK displays more thermal stability than PEKK. Table II summarizes the solubility of PEKK and CPEKK in organic solvents. It shows that PEKK has excellent solubility in most solvents, while CPEKK is less soluble than PEKK in N, N-dimethylacetamide (DMAc), CHCl₃, N, N-dimethylformamide (DMF), and o-dichlorobenzene (o-DCB). It is probably caused by the change in polarity and regulation of polymer chain because carbonyl was converted into less polar and more regular pyrazine after cyclization.

In addition, when we changed the sequence of cyclization and polymerization (Scheme IV), the attempt to get polymer with high molecular weight failed. After DFKK is cyclized into derivative of pyrazine, weaker electron-drawing ability of pyrazine moiety weakens the reactivity of new difluoride.

CONCLUSIONS

4,5-Bis(4-fluorobenzoyl)-1-methylcyclohexene (DFKK) has been prepared, which undergoes reaction with 2,2-(*p*-hydroxyphenyl)-*iso*-propane to give poly(ether ketone ketone). The polymerization reaction that was conducted in sulfolane in the presence of K₂CO₃ gives high molecular weight polymer. The poly(ether ketone ketone) has the properties of excellent solubility, high heat resistance, and good tensile strength. CPEKK, as the ring-closing product of PEKK with hydrazine, is more thermally stable and less soluble.

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REFERENCES

- Lindfors, B. E.; Mani, R. S.; McGrath J. E.; Mohanty, D. K. *Makromol Chem Rapid Commun* 1991, 12, 337–345.
- Wallace, T. J.; Schriesheim, A. *Tetrahedron Lett* 1963, 17, 1131–1137.
- Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R. J.; Rose, J. B.; Staniland, P. A. *Polymer* 1981, 22, 1096–1103.
- Bishop, M. T.; Karasz, F. E.; Russo, P. S.; Langley, K. H. *Macromolecules* 1985, 18, 86–93.
- Yang, H.; Sargent, J. R.; Hay, A. S. *J Polym Sci Part A* 1995, 33, 989–997.
- Meng, Y.; Hill, A. R.; Hay, A. S. *J Polym Sci Part A* 1999, 37, 1781–1788.
- Gao, Y.; Dai, Y.; Jian, X.; Peng, S.; Xue, J.; Liu, S. *Acta Polym Sinica* 2000, 3, 271–274.
- Rose, J. B.; Staniland, P. A. U.S. Patent 4320224, 1982–3–16.
- Meng, Y. Z.; Hay, A. S.; Jian X. G.; Tjong S. C. *J Appl Polym Sci* 1998, 68, 137–143.
- Guo, Q. P.; Huang J. Y.; Chen, T. *J Appl Polym Sci* 1991, 42, 2851–2853.
- Wham, G. K.; Hay A. S. *Polym Prepr* 1991, 32, 389–390.
- Yoshida, S.; Hay, A. S. *Macromolecules* 1995, 28, 2579–2581.
- Keitoku, F.; Kakimoto, M.; Imai, Y. *J Polym Sci Part A* 1994, 32, 317–322.
- Zolotukhin, M. G.; Dosieret, M.; Fougnes, C.; Villers, D.; Gileva, N. G.; Fatykhov, A. A. *Polymer* 1995, 36, 3575–3583.
- Wu, C.; Bo, S.; Siddiq, M.; Yang, G.; Chen, T. *Macromolecules* 1996, 29, 2989–2993.
- Wang, F.; Roovers, J. *Macromolecules* 1993, 26, 5295–5302.
- Xuan, Y. N.; Jian, X. G.; Xu, Z. Y. *Chin Chem Lett* 1999, 10, 1013–1014.
- Peng, J.; Jian, X. G.; Li, Q.; Xin, X. L.; Gu, B. *Acta Polym Sinica* 2000, 3, 354–357.
- Adams, R.; Geissman, T. A.; *J Am Chem Soc* 1939, 61, 2083–2089.
- Singh, R.; Hay, A. S. *Macromolecules* 1992, 25, 1017–1156.