Rheological studies on novel high performance polyarylethersulfones

Donghong Yu[*1], Kristian Keiding[1], Søren Hvidt[2]

[1]Section of Chemistry, Department of Life Sciences, Aalborg University, Denmark
[2]Department of Chemistry, Roskilde University, Denmark

ABSTRACT
The flow properties of three different synthesized series of random copolymers of poly(aryl ether sulfone) (PES), poly aryl ether ether sulfone (PEES), and poly aryl ether biphenyl ether sulfone(PEBES) have been studied. The dependence of the glass transition temperature (T_g) on the chemical structure is explored. The rheology studies are done as functions of copolymer compositions at different temperatures above T_g.

INTRODUCTION

In recent years there has been growing interest in the development of high performance polymers for the aerospace, electrical, and automobile industries. Such polymers are technologically important, with applications such as composite matrices, high temperature films, adhesives, and cable insulation. The high performance plastics generally exhibit outstanding high temperature stability, excellent mechanical properties, and radiation and hydrolytic stability. The known example is the poly(arylene ether)s or PAEs such as poly(arylene ether sulfone), i.e., PAES or PES[1,2]. The molecular chains in these series of polymers contain rigid aromatic rings which give them very high glass transition temperatures(T_g) and superior dimensional stabilities, e.g., T_g of PES is 225°C[4]. Some modified PAEs which may be used at a temperature up to 260°C[3-6] have been synthesized. A great deal of effort has been expended in developing new high performance PAEs with high heat resistance. These efforts have, however, been focused on various homopolymers. In this paper, several series of poly(phenylene ether sulfone) containing random copolymers have been synthesized for this study and the relaxational and rheological properties of these novel copolymers were studied in detail.

EXPERIMENTAL

Material Both monomers of 4,4'-Dihydroxybiphenyl (or 4,4'-Biphenol), Bis(4-hydroxyphenyl) sulfone (BHPS), Bis(4-chlorophenyl) sulfone (BCPS) and solvent of diphenyl sulfone were provided by the Xinghua Chemical Plant of the Jilin University (China). The three monomers and the solvent were purified by re-crystallization from ethanol and acetone, respectively. 1,4-benzenediol (Hydroquinone), K_2CO_3 and Na_2CO_3 from Aldrich were directly used without any further purifications.

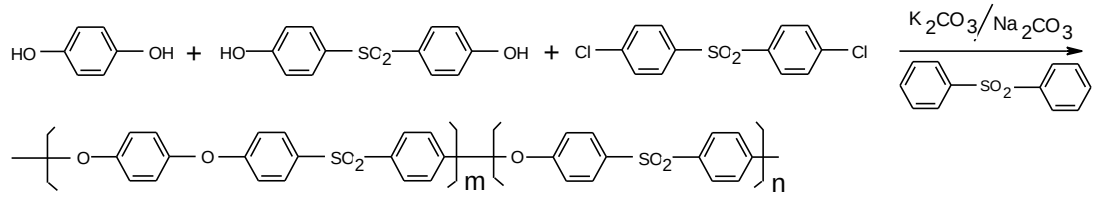
Polymerization Random copolymers of poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene)-co-poly(oxy-1,4-phenylene-oxy-1,4-phenylenesulfonyl-1,4-phenylene) or (PEES-co-PES), poly (oxy-1,4-biphenylene-oxy-1,4-phenylenesulfonyl-1,4-phenylene)-co-poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) or (PEBES-

* To whom correspondence should be addressed

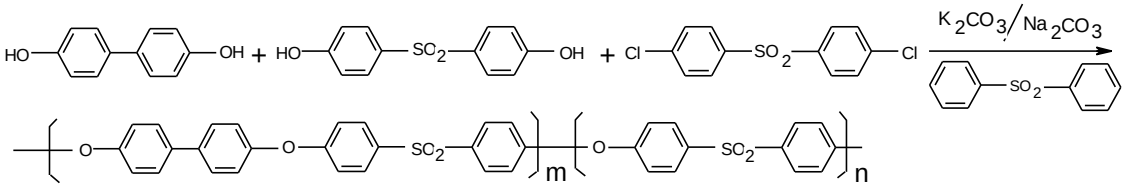
co-PES), and poly (oxy-1,4-phenylene-oxy-1,4-phenylenesulfonyl-1,4-pheny lene)-co-poly(oxy-1,4-phenylene sulfonyl-1,4-phenylene) or (PEBES-co-PEES) were produced by using Hydroquinone, Biphenol, BHPS, and BCPS as comonomers with different molar ratio in order to achieve different series of copolymers with different compositions. Polymerization was done by using diphenyl sulfone as a solvent at 20 wt/wt % solid content in the presence of K_2CO_3 and Na_2CO_3. The primary and secondary deprotonation occurred at 180°C and 250°C respectively, lasting 3 hours. The prepolymerization step was kept for 2 hours at 290°C, the final polymerization was made at 310°C for another 2 hours. The product was refluxed with water repeatedly to remove NaCl and KCl, then it was subjected to soxhlet extraction with acetone in order to remove the solvent. Finally all products were dried under vacuum at 100°C for 12 hours. Further information will be found out in articles published elsewhere[7].

Rheological measurements A XLY-II capillary rheometer (Scientific Instrumental Factory of Jilin Univeristy, China) was employed to perform the rheological characterization using a 5-mm long and 1-mm diameter capillary (L/*D* = 5) at different temperatures ranging from 310°C to 375°C. The samples were added into the capillary and kept in the melt for 5 minutes before testing. Rabinowitsch correction and entrance effect were taken into consideration because of the short capillary employed. With different controlled pressure drops, the piston speed was directly measured, afterwards the corresponding volumetric flow rates Q could be derived from it. Then the apparent wall shear stress is given by: $s = \frac{\Delta P}{2\left(\frac{L}{D} + e\right)}$, where, ΔP is the pressure drop, and e is the Bagley correction factor from a plot of ΔP as a function of L/D in order to account for the entrance effect. The apparent shear rate was denoted by $\dot{g}_{app} = \frac{4Q}{pD^3}$, Rabinowitch correction was then made by plotting $\log\dot{g}_{app}$ versus logσ, therefore the true shear rates could be obtained by equation $\dot{g} = \frac{1}{4}\left(3 + \frac{d(\log\dot{g}_{app})}{d(\log s)}\right)\dot{g}_{app}$. Finally the viscosity was calculated by $h = \frac{s}{\dot{g}}$.

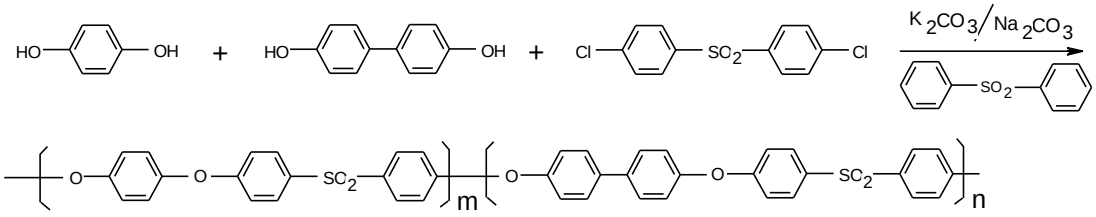
Viscosity in solutions The inherent viscosities(η_{IV}) of the three series of copolymers were determined using an Ubbelohde viscometer at a concentration of 0.1g/dL in concentrated sulfuric acid (98%) at 25.00 ± 0.10°C, $h_{IV} = \frac{1}{c}\ln\left(t/t_0\right)$, where c=0.01g/10ml, t and t_0 is the flow time of solution and solvent, respectively.



A: PEES-co-PES



B: PEBES-co-PES



C: PEBES-co-PEES

Scheme 1. Structure of the copolymers of PES, PEES and PEBES: A). Series random copolymer of PEES and PES; B). Series random copolymers of PEBES and PES; C). Series random copolymers of PEBES and PEES

Table 1. The composition of different series of copolymers

PEES-PES	Series names	A1	A2	A3	A4	A5
	(PEES) mol %	20	40	60	80	100
	(PES) mol%	80	60	40	20	0
	InherentViscosity(dL/g)	0.86	1.12	0.97	0.85	0.68
PEBES-PES	Series names	B1	B2	B3	B4	B5
	(PES) mol%	20	40	60	80	100
	(PEBES) mol%	80	60	40	20	0
	InherentViscosity(dL/g)	0.65	0.79	0.82	0.60	0.69
PEBES-PEES	Series names	C1	C2	C3	C4	C5
	(PEBES) mol%	20	40	60	80	100
	(PEES) mol%	80	60	40	20	0
	InherentViscosity(dL/g)	0.59	0.68	0.80	0.63	0.70

Glass transition temperature The glass transition temperatures were determined using a Perkin–Elmer differential scanning calorimeter (model DSC-7) at a heating rate of 10°C/min under a nitrogen flow, and the reported T_g values were

recorded from the second scan after the first heating and quenching.

RESULTS AND DISCUSSION

Polymerization Three series copolymers were prepared via nucleophilic polycondensation in the presence of anhydrous K_2CO_3 and Na_2CO_3 as catalyst for the deprotonation of the hydroxy group ending monomers. The synthetic scheme is shown in Scheme 1, and the detailed procedure is outlined in the Experimental section. Table 1 shows the compositions of these three series of copolymers. The chain flexibility/rigidity of the copolymers listed in Table 1 depends on the molar ratios PEES, PES, and PEBES. The fairly high inherent viscosities summarized in Table 1 indicate that the copolymers have high molar masses. Shorter oligomers can be obtained using a relatively short polycondensation time since molar masses increase with increasing reaction time for polycondensation systems. Based on the similar reactivities of nucleophilic substitution for alkyl oxide groups attacking the Biphenol, Hydroquinone, and BHPS, backbone structure is most probably random. Unfortunately neither their chain sequences nor molecular masses could be investigated due to their limited solubilities.

Relaxation Figure 1 shows the variation of glass transition temperature with the molar ratio between - SO_2- and - O - bonds in the backbone of these 2 series of PEES-co-PES and PEBES-co-PES copolymers. When the molar contents of BHPS or Biphenol are 100 mol% and 0 mol% respectively, the samples are homopolymers of either or the three starting materials, PEES, PES and PEBES. It can be seen that T_g increases with the increase of - SO_2- content. This can mainly be attributed to the rigidity of the sulphonyl groups in the main chain. The degree of free rotation of single bonds between C and S from - SO_2- is much less than that of C-C bonds. Their chain conformations do not vary too much.

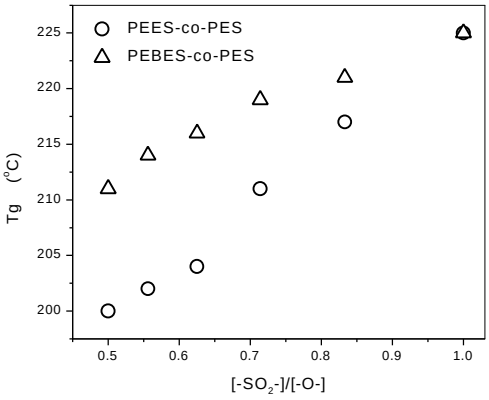


Figure 1. Relationship between glass transition temperature and molar ration of sulphonyl and ether groups in the backbone of copolymers of (o)PEES-co-PES, (Δ)PEBES-co-PES

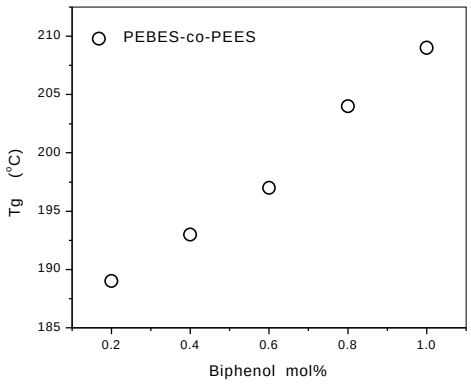


Figure 2. Biphenol content dependent on glass transition temperature of (o)PEBES-co-PEES random copolymers

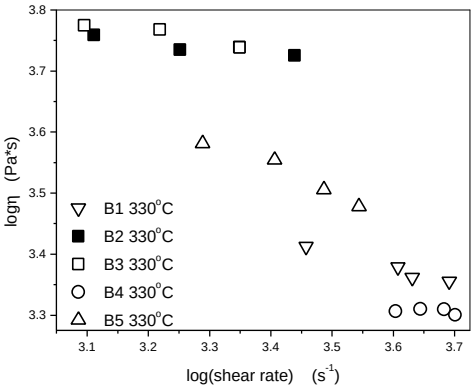


Figure 3. Melt viscosity versus shear rate for PEES-co-PES

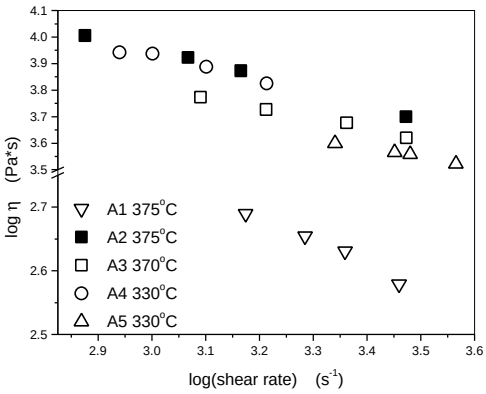


Figure 4. Melt viscosity versus shear rate for PEBES-co-PES

As the chain rigidity increases the segment relaxation time. Furthermore, the more -O- bonds there are, the more flexible the backbone. This is caused by the higher degree of rotational freedom of the C-O single bond than the C-C bond. On the other hand, the more sulphonyl groups, the higher dipole-dipole intra-molecular interactions they might have. Meanwhile, it has been found that the decrease of T_gs of PEBES-co-PES is not as sharp as that of PEES-co-PES. This is because at the same time the numbers of more rigid biphenyl groups also increase. The final effect reflects the competition. Therefore, the T_gs of the copolymers can be tailored by changing the molar ether or biphenyl content. The analysis of T_g of PEBES-co-PEES as a function of biphenol's molar percentage is illustrated in Figure 2. When the [-SO_2-]/[-O-] ratio was kept constant at 0.5, it shows that the T_gs of this series of copolymers increases with the increasing of biphenyl contents. This implies that the rigidity of biphenyl groups plays a more important role than the flexible ether bonds do.

Rheology The shear rate dependence of the melt viscosity of PEES-co-PES, PEBES-co-PES and PEBES-co-PEES can be seen in Figure 3, 4, and 5. The results indicate that the viscosities tend to decrease with increasing shear rates. All of the copolymers demonstrate a clear pseudoplastic or shear-thinning behavior, which is general for most of the polymeric materials as Non-Newtonian fluids. In Figure 3, it is also seen that, for a given shear rate, the viscosity does not systematically depend on the composition of the copolymers, e.g., viscosity decrease as A2≥A4>A3≥ A5>A1. The molecular structure dependence of viscosities can not be concluded. This might be because of their noncomparable molecular weights. For modeling the fluid properties, logarithmic shear stress for the arbitrarily chosen sample A3 was plotted against the logarithmic shear rates at different temperatures, which can be seen in Figure 6. The relationship between the shear stress and shear rate in logarithmic scale of this sample at different temperatures can be approximated by a linear function. This has been also done on all the other samples (data not shown).

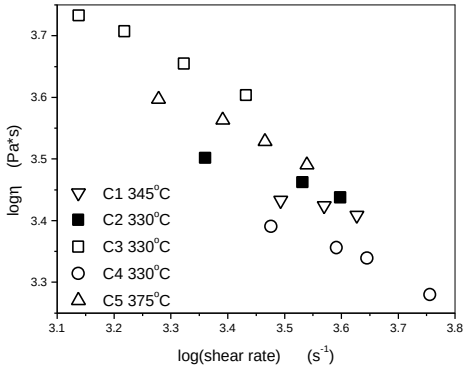


Figure 5. Melt viscosity versus shear rate for PEBES-co-PEES

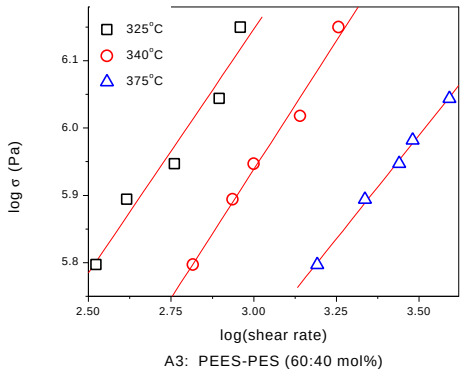


Figure 6. Shear stress of A3(PEES-co-PES) as a function of shear rates

One may also infer from Figure 3-5 the similar relationship for the other copolymers. A power relationship of the form of $s = k\dot{g}^{n}$ or $h = k\dot{g}^{n-1}$, (n is the power law exponents) is applicable for these copolymers. From the intercept of the logη versus log$\dot{g}$, the value of log$k$ can be obtained. Since $k = Ae^{\frac{\Delta E}{RT}}$, the apparent activation energy of the polymeric flow can be derived from the slope by linear fittings on a plot of ln$k$ versus 1/T. The activation energies of PEES-co-PES, copolymers are illustrated in Figure 7. From PES to PEES, the dependency of the melting viscosities on temperature becomes less pronounced as the copolymers' composition approach to PEES. This is due to the fact that the intramolecular forces get weak when the rigidity decreases as the - SO_2- content decreases, and, hence, the ΔE value decreases as well. The PEES segments in copolymers can act as plasticizers for the polymer melts, which can be used in controlling viscosities for extrusion or injection molding. This can be the guidance for the processing window of these kinds of copolymers.

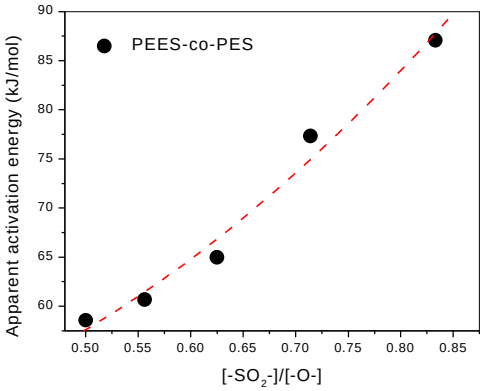


Figure 7. Activation energy of the different copolymers varying composition

CONCLUSIONS

Random copolymers of PES-co-PEES, PES-co-PEBES and PEES-co-PEBES are synthesized in the laboratory. From the relaxation behavior of polyarylene ether sulfones, the T_gs are influenced by the key factors of the ratio of sulphonyl and ether groups, the type of the aromatic. The rheological properties are also studied. All of these 3 series of copolymers behave as pseudoplastic Non-Newtonian fluids. They follow a power law. The Non-Newtonian exponent of them increases while the temperature raises. The lower the temperature is, the stronger Non-Newtonian properties they exhibit. The

apparent activation energy increases with their rigidity in the main chain.

ACKNOWLEDGEMENT
The authors would like to thank Morten L. Christensen, Yuanzheng Yue, and Erik A. Jensen for their help in writing this paper.

REFERENCES

1. Spricigo, C.B., Petrus, J.C.C, Machado, R.A.F. (2002), "Preparation and characterization of polyethersulfone membranes for use in supercritical medium", *J. Membrane Sci.* **205**, 273-278

2. Blinne, G., Knoll, M.,. Muller, D, and Schlichting, K. (1985), "Thermoplastic polyether sulfones-structure,properties and applications" *Kunststoffe,* **75**, 29.

3. Rao, V.L., Sabeena P.U., Rao,M.A. (1999), "Synthesis and Characterization of Poly(ether sulfone) and Poly(ether sulfone ketone) Copolymers", *J. Appl. Poly. Sci.* **73**, 2113-2121

4. Qipeng, G., Jinyu, H., and Tianlu, C. (1991), "The phase behavior of phenolphthalein poly(ether ether ketone) with poly(ethylene oxide)"**,** *J. Appl. Polym. Sci.*, **42,** 2851.

5. Zhang, H., Chen, T. and Yuan, Y. (1985) Chin. Pat. 85,108,751.5.

6. Zolotukhin, M.G. (1995), "Aromatic homopolymers obtained by precipitation polycondensations.1. Synehesis of naphthalene containing polyketones" *Polymer,* **36,** 3575.

7. a).Yu, D. et al, unpublished results; b). Hedrick J.L., Mohanty D.K., Hohnson B.C. (1986) "Radiation resistant amorphous all aromatic polyarlene ether sulfones-synthesis, characterization, and mechanical properties" *J. Polym. Sci. Poly. Chem.* **24**, 287-300