Polymer Bulletin 60, 785–789 (2008)
DOI 10.1007/s00289-007-0823-4

Polymer Bulletin

# Rheological response of mesophase transition of a main-chain liquid crystalline poly (aryl ether ketone)

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Received: 2 January 2007 / Revised version: 28 June 2007 / Accepted: 11 August 2007

## Summary

The lg *G*'-lg *G*" plot known as Han plot in dynamic rheological measurement was used in the characterization of the anisotropic-isotropic, *i.e* nematic-isotropic transition of a thermotropic liquid crystalline poly(aryl ether ketone) synthesized by copolymerization of 4,4'-biphendiol, 4,4'-difluobenzophenone and *t*-butylhydroquinone. Dynamic frequency sweeps were carried on Advanced Rheolmetric Expansion System to give lg *G*'-lg *G*" plots at different temperatures covering the whole temperature range from nematic phase to isotropic phase. It was found that the slopes of the Han plots gradually approach 2.46 with increasing temperature before reaching the isotropic point. In the isotropic phase the slopes become completely independent of temperature. Based on this observation, the nematic-isotropic transition is considered to be the temperature after which the slopes of the plots become constant, which is in our case 2.46.

## Introduction

The realization of liquid crystalline properties in super engineering plastic poly (aryl ether ketone)s is promising in solving problems associated with processing this kind of materials due to the significantly lower degree of crystallinity and melt viscosity of liquid crystalline polymers compared to their structurally similar counterparts [1]. As a processing-related and complementary technique of differential scanning calorimeter (DSC), polarized microscope (POM) and X-ray diffraction pattern (XRD) commonly used in the characterization of phase transition, dynamic rheological method has been utilized in characterizing liquid crystalline polymers including poly(aryl ether ketone)s and has afforded valuable information on the mesophase transition [2-9]. It has been proven in the literatures that, the rheological properties of multicomponent/ multiphase polymer systems are very much dependent on their morphological state which in turn can be determined by examining the rheological behaviors [10]. Han and co-workers have demonstrated that lg *G*' versus lg *G*" plots of a polymer (system) are very much sensitive to its morphological state and have made an observation on the relationship between the slops of lg *G*' *versus* lg *G"* plots and the morphological state of block copolymers and thermotropic liquid crystalline polyesters [5-8] in terms of the order-disorder transitions.

In the present paper, we report the dynamic rheological characterization of the nematic-isotropic transition of a thermotropic liquid crystalline poly (aryl ether ketone) by examining the slopes of lg *G*'-lg *G*" plots (known as Han plots) throughout the whole temperature covering the clearing point of the thermotropic liquid crystalline poly (aryl ether ketone) (TLCP PAEK) investigated.

## Experimental

The TLCP PAEK is a random copolymer of 4,4'-biphendiol, 4,4'-difluobenzophenone and *t*-butylhydroquinone with biphenol moiety of 70mol% (referred to as PAEK3 in this paper). PAEK3 has a nominal melting temperature $T_m$ of 330 °C, a nematic-isotropic transition temperature $T_i$ of 397 °C and decomposition temperature of 500 °C, as determined by DSC and TGA measurement. The details of the synthesis were previously reported elsewhere [1, 10, 11].

The dynamic rheological measurements were carried out on an ARES-9A (Advanced Rheolmetric Expansion System, Rheometric Scientific Inc, USA). Experimental parameters and conditions were described elsewhere previously [9]. In short, the parallel plate geometry with plate diameter of 25 mm was adopted. Dynamic storage modulus *G*' and loss modulus *G*" as a function of angular frequency ($\omega$) in the oscillatory shear mode at temperatures ranging from 330 °C to 410 °C were measured. At a given temperature a fixed strain was used for each rheological measurement. The dynamic frequency sweep was carried out from 0.1 rad/s to 100 rad/s. The strain was controlled to be in the range from 0.3% to 3% to ensure that the dynamic rheological experiment was carried out within the linear viscoelastic range and to maintain a large enough torque. First strain sweep was performed to get the maximum strain in the linear range. The gap between the two parallel plates was carefully adjusted to warrant the sample touch the plates well. At a certain temperature dynamic frequency sweep gives the plots of lg *G*' or lg *G*" *versus* frequency. All the rheological experiments were conducted under nitrogen atmosphere to avoid the oxidative degradation of the polymer.

A solvent-cast specimen of PEAK 3 was first heated to 410 °C, subjected to steady state shear flow at a very low shear rate for several minutes to eliminate all the previous thermal histories related to the sample preparation and then cooled slowly to a predetermined temperature, *i.e.* 400, 390, 380, or 370 °C before taking the dynamic rheological experiments.

## Results and discussions

Dynamic rheological technique has been used in addition to small angle X-ray diffraction and neutron scattering in the determination of order-disorder transition temperatures ($T_{ODT}$) of block polymers [12-14] and liquid crystalline polymers. Examples of findings include the three-region change in viscosity, *i.e.* viscosity decrease in both the nematic and isotropic phases but an increase in biphase approaching the mesophase transition with increasing temperature, a phenomenon not obeying the Arrhenius rule and relating to the mesophase transition [9,10,15]. Also as mentioned earlier, C.D. Han *et al* proposed the use of lg *G*'-lg *G*" plots as a means to determine the order-disorder transition.

Plots of lg *G'* versus lg *G"* of PAEK3 from dynamic frequency sweeps at different temperatures were shown in Figure 1.

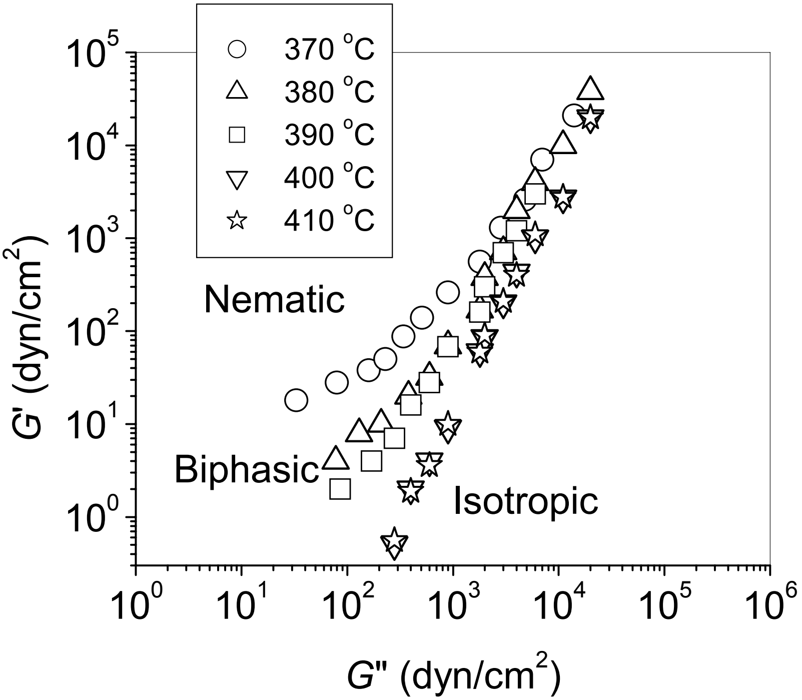

**Figure 1** Han plots for poly(aryl ether ketone) copolymer based on 30 mol% *t*-butylhydroquinone, 70 mol% 4,4'-biphendiol and 4,4'-difluobenzophenone, showing the change of the slopes as temperature gradually approaches the isotropic transition temperature.

It is seen from Figure 1 that in the nematic region, *i.e.* $T$<390 °C, the shape of the plots depends on temperature and has a slope far less than 2 in the low-frequency region. In the isotropic region, *i.e.* 400 and 410 °C, lg *G' versus* lg *G"* plots become independent of temperature and has a slope of 2.46. As the temperature increases in the nematic region, approaching the isotropic transition, the lg *G'*-lg *G"* plots gradually approach that for the isotropic phase, which is very similar to the observation made by Han and co-workers for a SI diblock copolymer. In other words, the slopes of lg *G'*-lg *G"* plots of PAEK3 vary with temperature in the liquid crystalline state to a certain critical value and then remain completely independent of temperature with further increasing temperature (with plots at 400°C and 410°C completely overlapped). The isotropic transition temperature $T_i$ was thus considered to be the temperature at which lg *G' versus* lg *G"* plots no longer vary as the temperature is increased above its melting point. The nematic-isotropic transition temperature obtained by this method is in good agreement with those obtained from POM observation and DSC measurement.

We also performed experiments on a structurally similar PAEK with 80mol% *tert*-butylhydroquinone, 20mol% biphenol and 1,4-bis(p-benzophone)benzene (sample was referred to as PAEK8) which exhibits no liquid crystalline properties to clarify if the above rheological behavior of PAEK3 is characteristic response of mesophase transition of liquid crystalline poly(aryl ether ketone)s. Results were shown in Figure 2.

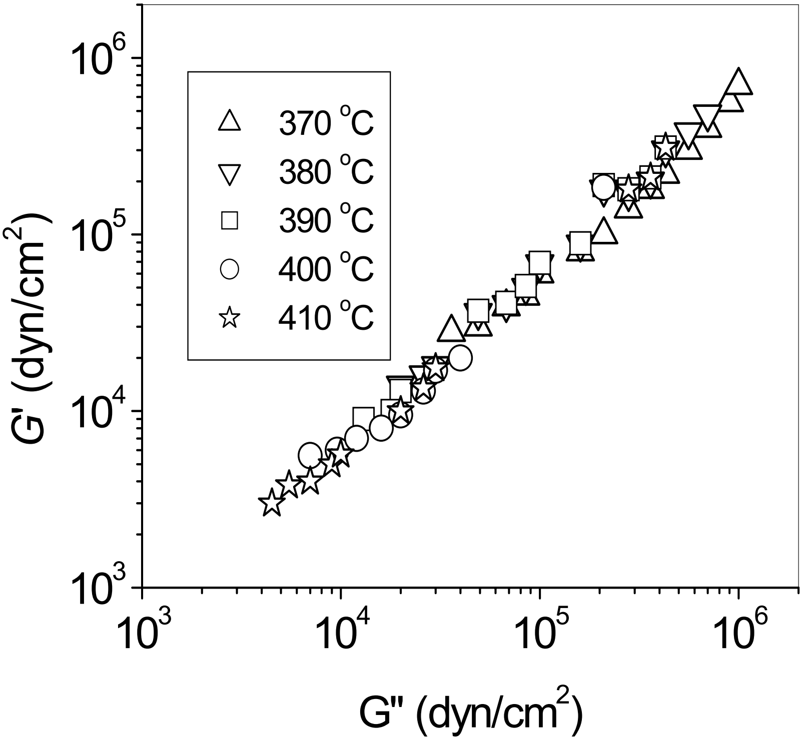

**Figure 2** Han plots for poly(aryl ether ketone) copolymer based on 80mol% t-butylhydroquinone, 20 mol% 4,4’-biphendiol and 4,4’-difluobenzophenone, showing no phase transition with the slopes of different temperatures being overlapped.

In contrast to Figure 1, plots at different temperatures for PAEK8 overlap each other well, showing no correlation between the slopes of plots with measophase transition, completely different from what is seen in Figure 1.

The above observation on Han plots indicates that the anisotropic-isotropic transition temperature of a TLC-PAEK can be obtained by examining the lg *G*’-lg *G*” plot. Han has pointed out that such a correlation of the slope of lg *G’*-lg *G*” plot with morphological state has a basis of molecular viscoelasticity theory, according to which lg *G*’-lg *G*” plots for homogeneous polymer systems are virtually independent of temperature [5-8, 14]. The lg *G*’-lg *G*” plots show little changes as long as the morphological state of a polymer changed little over the temperature range at which the rheological measurement was carried out. Linear viscoelasticity theory indicates a plot with slope of 2 for flexible monodispersed homopolymers [16], while the above experiments give a slope of 2.46 for PAEK3. This variation could possibly be attributed to the polydispersity nature of the copolymer investigated which was synthesized *via* solution polycondensation.

## Conclusions

We have correlated Han plots of a thermotropic liquid crystalline poly(aryl ether ketone) with its mesophase transition, and have obtained the temperature of anisotropic-isotropic transition *i.e.* nematic-isotropic phase transition which is in good agreement with that obtained by traditional optical and calorimetric methods. This indicates seemingly a broad applicability of dynamic rheological technique in the characterization of order-disorder transition. Its potential use in characterization of transition of phase with long-range positional order, *i.e.* smectic phase of poly (aryl ether ketone) with other moieties of *tert*-butylhydroquinone calls for a further investigation.

*Acknowledgements.* Prof. Qiang Zheng at Department of Polymer Science and Engineering, Zhejiang University, China, is gratefully acknowledged for having given access to experimental facilities and for interesting discussions.

## References

1. Bennett GS, Farris RT, (1994) Polym. Eng. Sci. 4: 761
2. Wissbrun KF, Griffin AC, (1982) J. Polym. Sci., Polym. Phys. 20: 1835
3. Blumstein A, Thomas O, Kumar S, (1986) J. Polym. Sci., Polym. Phys. 24: 27
4. Kumar RS, Clough SB., Blumstein A, (1988) Mol. Cryst. Liq. Cryst.,157: 387
5. Han CD, Kim J, (1987) J. Polym. Sci.: Polym. Phys. 25(8): 1741
6. Han CD, Kim J, Kim JK, (1989) Macromolecules 22: 383
7. Han CD, Baek DM, Kim JK, (1990) Macromolecules 23: 561
8. Han CD, Kim J, (1993) Polymer 34: 2553
9. Sun H, Wang FH, Jiang ZH, Zhang WJ, Wu Z.W, (2001) J. Mater. Sci. Lett. 20: 1117
10. Zhang SJ, Zheng YB, Wu Z W, (1997) Chem. J. Chin. Univ.18: 367
11. Sun H, Na H, Wu ZW, (2000) Polym. Int., 49: 1539
12. Bates FS, Rosedale JH, Fredrickson G H, (1990) J. Chem. Phys. 92: 6258
13. Adams JL, Register RA, (1994) Macromolecules 27: 6026
14. Yamaguchi D, Hashimoto T, Han CD, (1997) Macromolecules 30: 1621
15. Kim SS., Han CD. (1994) J. Polym. Sci.: Polym. Phys. 32(2): 371
16. Han CD, John MS., (1986) J. Appl. Polym. Sci. 32: 3809