Macromolecular Research, Vol. 24, No. 2, pp 182-187 (2016)
DOI 10.1007/s13233-016-4025-5

www.springer.com/13233
pISSN 1598-5032 eISSN 2092-7673

Molecular Consideration on the Lyotropic Liquid Crystalline Behavior of Poly(2-cyano-*p*-phenylene terephthalamide) Solutions in *N*-Methyl-2-pyrrolidone/Calcium Chloride

Dae Eon Jung[1], **Youngho Eom**[1], **Hu Young Yoon**[1], **Jaeyoung Lee**[2], **and Byoung Chul Kim**[*,1]

[1]*Department of Organic and Nano Engineering, Hanyang University, Seoul 04763, Korea*
[2]*Fundamental Technology R&D Group, Central Research Park, Kolon Industries, Inc., Gumi, Gyeongbuk 39366, Korea*

Received October 8, 2015; Revised December 9, 2015; Accepted December 19, 2015

Abstract: The lyotropic liquid crystalline behavior of poly(2-cyano-*p*-phenylene terephthalamide) (CY-PPTA) solution in the mixture of *N*-methyl-2-pyrrolidone and calcium chloride was investigated in terms of concentration and temperature. The intrinsic viscosity was decreased with increasing temperature, indicating the contraction of CY-PPTA chain at higher temperature. In dynamic viscosity measurement, the critical concentration (C^*) where phase transition to the liquid crystalline phase takes place was decreased with increasing temperature. Above the C^*, the dynamic viscosity was decreased and Bingham behavior got more noticeable with increasing concentration due to the development of the liquid crystalline structures. However, Bingham behavior was more notable at higher temperature at a given concentration. The viscosity curves showed the three distinct flow regions suggested by Asada and Onogi and negative first normal stress difference was observed in the range of intermediate shear rates.

Keywords: *para*-aramid, lyotropic, poly(2-cyano-*p*-phenylene terephthalamide), rheology.

Introduction

Para-aromatic polyamides (*p*-aramids) have been used in the production of high performance fibers because of their strong intermolecular interactions and inherent rigidity of molecular structure.[1-3] One of the typical success of the *p*-aramids is poly(*p*-phenylene terephthalamide) (PPTA), so-called Kevlar™ (Dupont, USA). Since it shows a very limited solubility to most of organic solvents, concentrated sulfuric acid has been uniquely used as the solvent for PPTA. Due to environmental problems and complicated equipment required in using sulfuric acid, there have been many attempts to make organo-soluble *p*-aramids by introducing large atoms or bulky groups to benzene rings.[4-16] Poly(2-cyano-*p*-phenylene terephthalamide) (CY-PPTA) is one of promising organo-soluble *p*-aramids and exhibits the lyotropic liquid crystalline behavior in organic solvent systems such as *N*-methyl-2-pyrrolidone (NMP)/calcium chloride ($CaCl_2$).[17-19]

The liquid crystalline behavior of a polymer was first explained by Flory (1956) who calculated critical volume fraction to form the liquid crystalline phase in relation with the aspect ratio of a rod-like molecule by assuming an athermal system.[20] However, there exist physical interactions between polymer molecules in real polymer solution systems. Thus, Maier and Saupe (1960) considered the degree of orientation-dependent interactions between polymer molecules to make up the weakness.[21] Although they widen the application of the prediction to the thermal systems, they simply covered van der Waals interactions. However, most *p*-aramids possess a strong intermolecular interactions through hydrogen bonding. Up to now, little literature is available on the analysis of liquid crystalline polymer reflecting such strong specific interactions. Recently, Eom and Kim (2014) reported the effects of strong physical interactions between cyano groups in polyacrylonitrile solution on phase change behavior.[22] The pendant cyano groups in CY-PPTA solution seem to play a significant role in the liquid crystalline behavior as well.

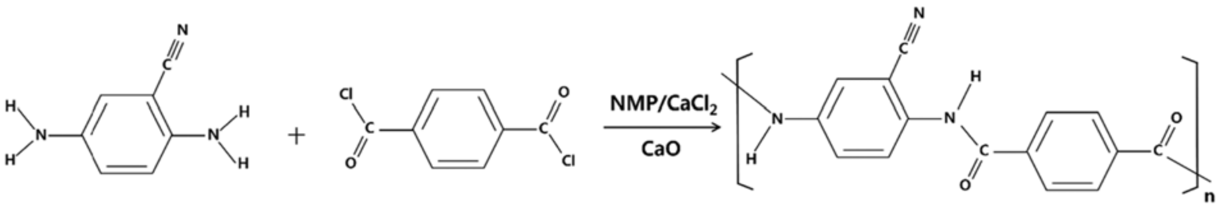
In this study, we tried to find out the effects of pendant cyano groups with high polarity on the phase transition of CY-PPTA solution. Among organic solvent systems, NMP/$CaCl_2$ system was selected because it has a strong potential to be used as the polymerization solvent of CY-PPTA for *in situ* fiber spinning. Thus, we rheologically investigated the liquid crystalline behavior of CY-PPTA solutions in NMP/$CaCl_2$ in terms of concentration and temperature.

Experimental

Materials. Terephthaloyl chloride (TPC) and calcium oxide (CaO) were purchased from Aldrich Co. (USA). TPC was

---

*Corresponding Author. E-mail: bckim@hanyang.ac.kr



Scheme I. The synthesis procedure of CY-PPTA.

purified by vacuum distillation. NMP was purchased from Daejung Chemicals Co. (Korea) and used without further purification. $CaCl_2$ purchased from Junsei Chemical Co. (Japan) was vacuum dried a week before use.

Preparation of CY-PPTA Solutions. CY-PPTA solution was prepared by polycondensation of TPC and 2-cyano-1,4-phenylenediamine (CYPPD) in NMP containing $CaCl_2$. The synthesis procedure of CY-PPTA is shown in Scheme I. Firstly, $CaCl_2$ was dissolved in NMP under nitrogen purging, followed by the addition of CYPPD. After CYPPD was completely dissolved, TPC was added with vigorous stirring. After the completion of polymerization, CaO was added to neutralize the system. Then, a CY-PPTA solution of 15 wt% was obtained.

Dilute CY-PPTA solutions of 0.01 to 0.3 g/dL and concentrated CY-PPTA solutions of 2 to 14 wt% were prepared by adding additional solvent to the 15 wt% solution, followed by stirring 2 days at 25 ºC.

Measurement of Physical Properties. The reduced viscosity (η_{red}) and specific viscosity (η_{sp}) was measured by Ubbelohde viscometer (Schott Co., Germany) over the concentration and temperature ranges, 0.01 to 0.3 g/dL and 30 to 60 ºC, respectively.

The rheological properties were measured by Advanced Rheometric Expansion System (ARES, TA instruments, USA). Parallel plate geometry was adopted whose diameter and gap were 50 and 0.8 mm, respectively. The steady shear mode was adopted with the shear rate range of 0.05 to 200 s^{-1}. The solutions were stabilized on the plate for 30 min at a given measuring temperature of 30 to 60 ºC to fully relax the residual stress.

The liquid crystalline textures of CY-PPTA solutions were observed by polarized optical microscope (Olympus BX51, Japan) equipped with CCD camera (Olympus DP70, Japan). The solutions were placed on a heating stage (Mettler Toledo FP-82HT, Switzerland) for 10 min to stabilize before measurement.

Results and Discussion

The reduced viscosity (η_{red}) of CY-PPTA solutions is plotted against concentration in Figure 1. The η_{red} is linearly increased with increasing concentration at a given temperature as expected. This means that a single molecular behavior is dominant without any specific intermolecular interactions. The intrinsic viscosity ([η]), a measure of coil dimension of a polymer in a solvent, can be obtained by extrapolating the η_{red} curve to zero concentration.[23,24] The [η] values are also shown in the left side of the figure. The [η] is decreased with increasing temperature, indicating a smaller hydrodynamic volume of CY-PPTA chains at higher temperature. That is, more dominant intramolecular interactions lead to the contraction of CY-PPTA chain at higher temperature, which is an indicative of a lower critical solution temperature (LCST) behavior.[22,25,26]

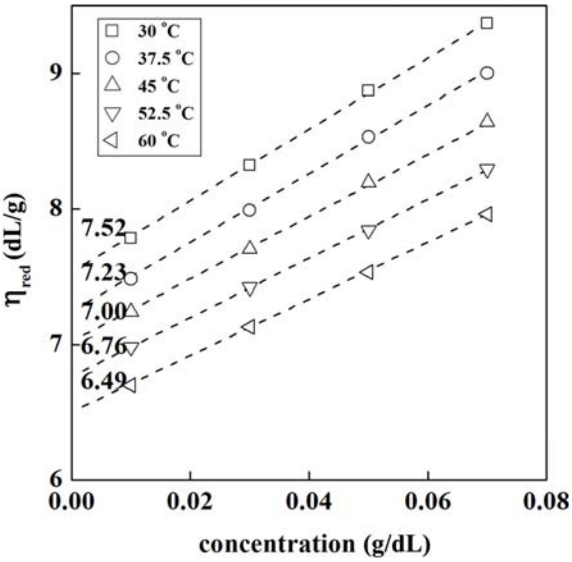


Figure 1. Plot of reduced viscosity (η_{red}) against concentration for CY-PPTA solutions.

The LCST behavior is ascribed to the effects of pendant cyano groups on the resonance structure and intramolecular interactions of CY-PPTA chains. In fact, the linearity of *p*-aramid chain largely originates from the resonance of amide group by delocalization of lone electron pairs in nitrogen.[27,28] However, cyano group disturbs this resonance. As shown in Figure 2, cyano group withdraws lone electron pairs in nitrogen of amide group through the resonance. Strong electronegativity of cyano group intensifies the electron-withdrawing by inductive effect. As a result, the C-N bond of amide group gives more single bond character. In other words, CY-PPTA chains would deviate from the linearity.

The curvature on CY-PPTA chains may offer more favorable conditions for intramolecular interactions. It was reported that highly polar cyano groups in a solution interact each other by polarizing polar solvent molecules in the form of a solvent bridge between them.[22] Intramolecular solvent bridge in CY-PPTA chain is schematically suggested in Scheme II.

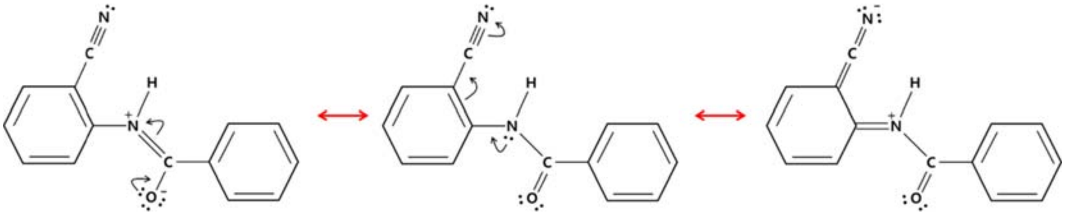
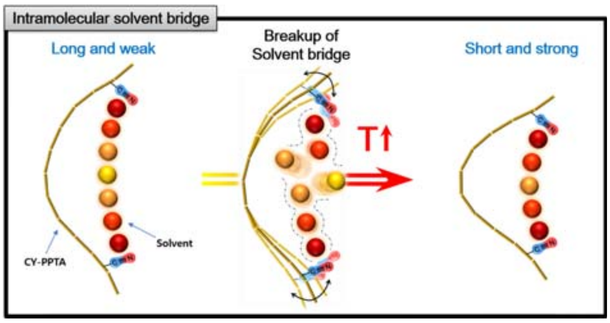


Figure 2. Electron dot diagrams of resonance structure of CY-PPTA chain.



Scheme II. The reduction mechanism of hydrodynamic volume at higher temperature; CY-PPTA chains are denoted as yellow rods and solvent molecules as spheres. The more strongly polarized solvent molecule is denoted as the deeper red colored one.

As temperature increases, more vigorous thermal motion of CY-PPTA chain makes the bridge unstable so the bridge is broken up by escaping less strongly polarized solvent molecules first.[22] That is, trade-off effect between entropy and enthalpy happens. Then much stronger solvent bridge with shorter equilibrium length is formed at higher temperature as shown in Scheme II. This leads to the decrease of end-to-end distance of the chain together with the decrease of its hydrodynamic volume. Consequently, polar pendant group brings about the unusual temperature dependence of CY-PPTA solutions.

Individual CY-PPTA chain starts to overlap with other chains when concentration is further increased. Figure 3 shows the specific viscosity (η_{sp}) of CY-PPTA solutions as a function of coil overlap parameter ([η]c), an index of the total volume occupied by a polymer.[29-32] The η_{sp} curves exhibit almost a single curve up to [η]c of one. Above that, the slope abruptly increases due to intermolecular diffusion of CY-PPTA chains. Then, highly polar cyano groups in other chains would polarize solvent molecules between them, producing intermolecular solvent bridges as depicted in Scheme III(a). In Figure 3, however, slope deviation is more noticeable at higher temperature, representing much stronger intermolecular interactions. At higher temperature, more frequent inter-diffusion of the chains weakens the solvent bridges and breaks them up. Thus much shorter and stronger bridges are formed as shown in Scheme III(a). These physical interactions are very strong and sometimes irreversible so it seems that CY-PPTA chains coalesce each other at higher temperature.[22]

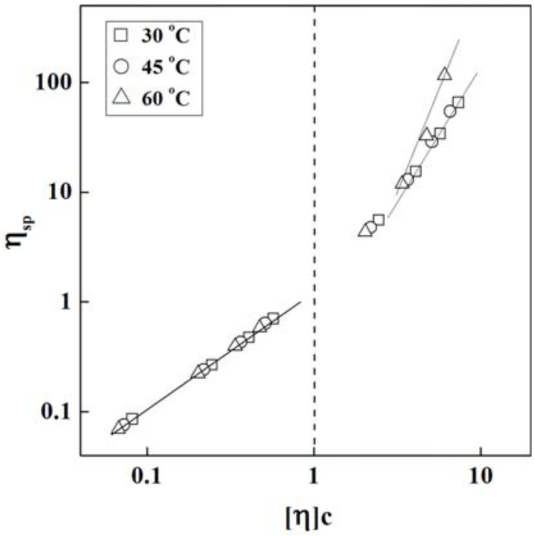
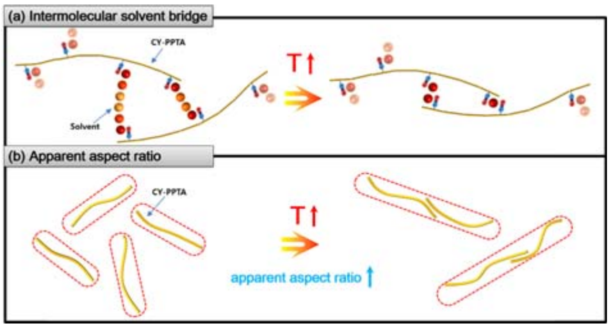


Figure 3. Plot of specific viscosity (η_{sp}) against coil overlap parameter ([η]c) for CY-PPTA solutions from 0.01 to 0.9 g/dL.



Scheme III. The effect of increasing temperature on the (a) intermolecular solvent bridge between pendant cyano groups and (b) apparent aspect ratio; CY-PPTA chains are denoted as yellow rods and solvent molecules as spheres. The more strongly polarized solvent molecule is denoted as the deeper red colored one.

Due to anisotropic molecular structure of CY-PPTA chains, the coalescence of CY-PPTA chains at higher temperature directly brings about enlargement of apparent aspect ratio as shown in Scheme III(b). According to partition function, a rod-like molecule with higher aspect ratio aligns at lower concentration to the liquid crystalline structure.[20] Figure 4 shows the critical concentration (C*) curves of CY-PPTA solutions. As expected, the C* is decreased with increasing temperature.

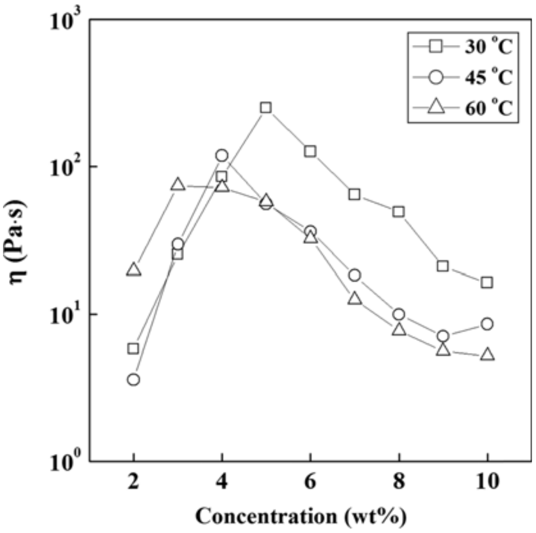


Figure 4. The critical concentration curves of CY-PPTA solutions at 1.0 s^{-1}.

Consequently, the C^* of a liquid crystalline polymer with strong physical interactions is largely affected by apparent aspect ratio rather than the aspect ratio of individual chains.

The shear viscosity curves of representative anisotropic CY-PPTA solutions are shown in Figure 5. The 5 wt% solution shows slight lower Newtonian flow region at 30 °C but noticeable Bingham behavior at 45 and 60 °C in Figure 5(a). Disappearance of lower Newtonian flow region means the existence of physical structures in a solution.[25,33] The liquid crystalline domains can act as Bingham bodies but, judging from the result at 30 °C, the concentration is too low to develop sufficient liquid crystalline structures. Then it can be said that physical structures other than liquid crystalline domains are strongly formed at higher temperature. That is, isotropic portion in biphasic CY-PPTA solutions would form three-dimensional physical networks connected by short solvent bridges at higher temperature.

The 9 wt% solution gives lower viscosity and more prominent Bingham behavior compared to the 5 wt% solution in Figure 5(b). This is due to the development of the liquid crystalline structures with increasing concentration. It is interesting to see that viscosity curves exhibit three distinct flow regions which is characteristic flow behavior of a liquid crystalline polymer suggested by Asada and Onogi.[34] In the Region 1, shear stress breaks up the piled polydomains into dispersed polydomains. The dispersed polydomains maintain their structures in Region 2 but finally are broken up to produce the monodomain continuous phase in the Region 3. In the figure, the Region 1 is less clearly observed at 30 °C. This means that the solution at 30 °C would not sufficiently produce the piled polydomains system. In other words, the liquid crystalline domains are more developed at higher temperature at a given concentration. In addition, it is worth noting that transition from the Region 2 to 3 takes place at lower shear rate at 30 °C.

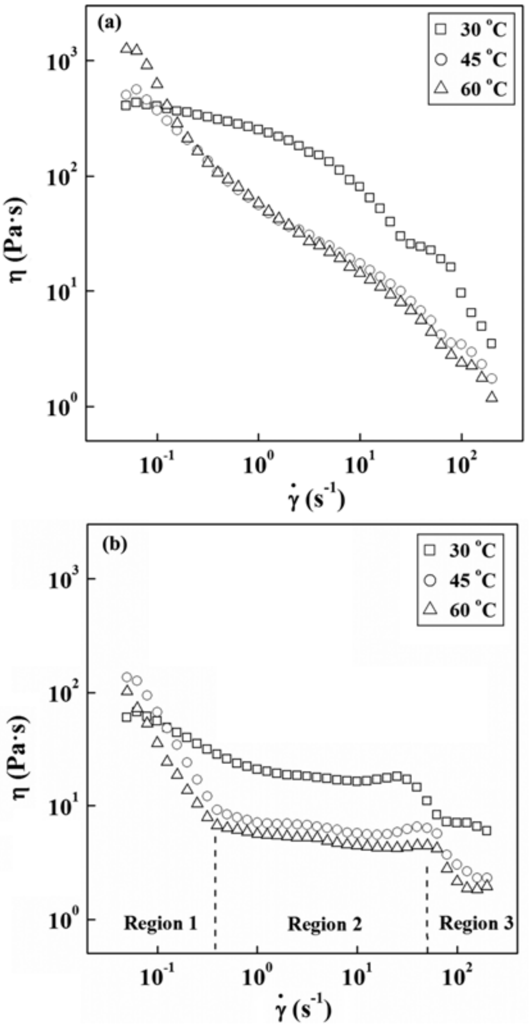


Figure 5. Plots of steady shear viscosity (η) *vs*. shear rate ($\dot{\gamma}$) for (a) 5 and (b) 9 wt% CY-PPTA solutions at 30, 45, and 60 °C.

This result suggests that the liquid crystalline domains at higher temperature is more durable on applied shear stress. CY-PPTA chains connected by the short solvent bridges seem to produce much stronger liquid crystalline domains at higher temperature.

The first normal stress difference (N$_1$) of 7 wt% CY-PPTA solutions is plotted against shear rate in Figure 6. Filled symbols stand for negative N$_1$ values which are converted to positive values for gaining logarithmic plot of N$_1$ curves. The N$_1$ curves show only positive values at 30 °C but negative values are observed in intermediate shear rate at higher temperature. It was reported that wagging behavior of directors in negative shear rate region connects unstable tumbling behavior of directors in low shear rate and stable flow behavior in high shear rate.[35-43] Fluctuations of directors originate from anisotropic molecular structure of a liquid crystalline molecule so it would highly depend on the aspect ratio of the liquid crystalline molecule. Hence, as previously mentioned, higher apparent

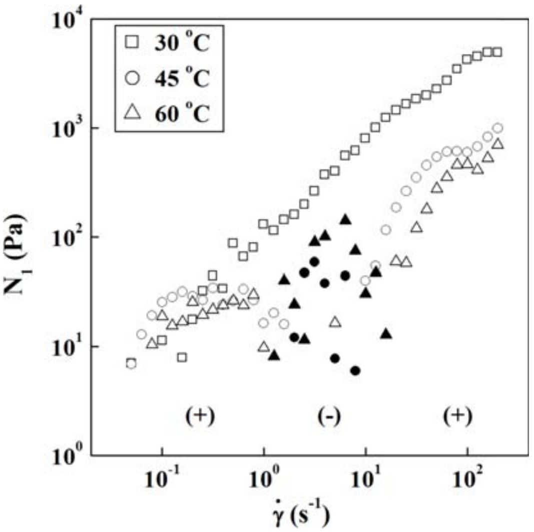


Figure 6. The first normal stress difference (N_1) values against shear rate ($\dot{\gamma}$) for 7 wt% CY-PPTA solutions. The positive values of N_1 are shown in open symbols while the negative values are in filled symbols.

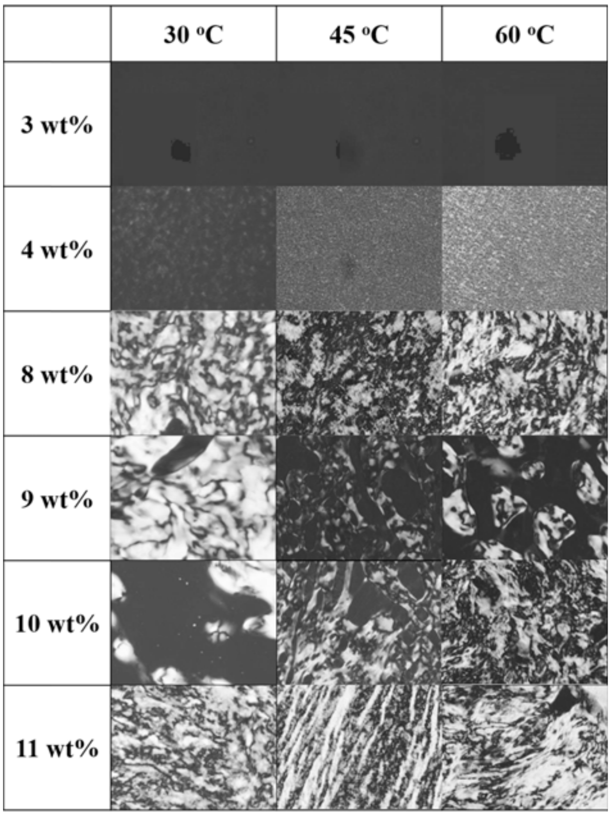


Figure 7. Polarized optical micrographs (100×) of CY-PPTA solutions at 30, 45, and 60 °C.

aspect ratio of CY-PPTA chains would result in more clear sign changes of N_1 curves at higher temperature.

The liquid crystalline behavior is clearly visualized by polarized optical microscope. In Figure 7, some faint liquid crystalline texture is detected at 4 wt% and gets more noticeable with increasing concentration. The representative texture of nematic phase, schlieren texture, starts to be observed at 10 wt% at 30 °C but 9 wt% at 45 and 60 °C. In principle, schlieren texture is developed when domains are well continuously arranged. Thus, this indicates that much more liquid crystalline domains are generated at higher temperature at a given concentration, which well coincides with the shear viscosity result.

Conclusions

Highly polar cyano groups as a pendant seemed to play a dominant role in intra- and inter-molecular interactions of CY-PPTA chains in polar solvent. Experimental results revealed that the physical interactions between CY-PPTA chains got more noticeable at higher temperature, indicating an LCST behavior. In addition, the formation of the liquid crystalline structure was observed at lower concentration at higher temperature, exhibiting the longer plateau region of Asada and Onogi model in the viscosity curve. Thus careful consideration of strong specific intermolecular interactions between rigid chains is recommended to understand flow behavior of a liquid crystalline polymer.

Acknowledgment. This work was supported by the Industrial Strategic Technology Development Program (10042636, Development of para-Aramid Fibers Spinnable in Organic Solvent) funded by the Ministry of Trade, Industry and Energy (MOTIE) of Korea.

References

(1) S. V. Kotomin, *J. Thermoplast. Compos. Mater.*, **26**, 91 (2013).
(2) K. Naito, *J. Appl. Polym. Sci.*, **128**, 1185 (2013).
(3) C. Y. Yue, G. X. Sui, and H. C. Looi, *Compos. Sci. Technol.*, **60**, 421 (2000).
(4) T. I. Bair, P. W. Morgan, and F. L. Killian, *Macromolecules*, **10**, 1396 (1977).
(5) R. R. Burch, W. Sweeny, H. W. Schmidt, and Y. H. Kim, *Macromolecules*, **23**, 1065 (1990).
(6) E. Y. Chu, Z. S. Xu, C. J. M. Lee, C. K. F. Sek, Y. Okamoto, E. M. Pearce, and T. K. Kewi, *J. Polym. Sci. Part B: Polym. Phys.*, **33**, 71 (1995).
(7) C. de Ruijter, E. Mendes, H. Boerstoel, and M. Hassanzadeh, *Polymer*, **47**, 8517 (2006).
(8) V. Frosini, G. Levita, and E. Butta, *Polym. Eng. Sci.*, **19**, 56 (1979).
(9) M. Ghaemy, A. Masoumi, S. M. A. Nasab, and M. Hassanzadeh, *J. Appl. Polym. Sci.*, **127**, 3169 (2013).
(10) Y. Guan, Y. J. Zheng, J. X. Cui, and X. H. Wan, *Chinese J. Polym. Sci.*, **28**, 257 (2010).
(11) S. H. Hsiao, C. W. Chen, and G. S. Liou, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 3302 (2004).
(12) E. J. Vandenberg, W. R. Diveley, L. J. Filar, S. R. Patel, and H. G. Barth, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 3745 (1989).

(13) S. Viale, A. S. Best, E. Mendes, W. F. Jager, and S. J. Picken, *Chem. Commun.*, 1596 (2004).

(14) S. Viale, N. Li, A. H. M. Schotman, A. S. Best, and S. J. Picken, *Macromolecules*, **38**, 3647 (2005).

(15) S. Zulfiqar, I. Lieberwirth, Z. Ahmad, and M. I. Sarwar, *Polym. Eng. Sci.*, **48**, 1624 (2008).

(16) S. Zulfiqar, M. Rafique, M. S. Shaukat, M. Ishaq, and M. I. Sarwar, *Colloid Polym. Sci.*, **287**, 715 (2009).

(17) S. L. Kwolek, P. W. Morgan, J. R. Schaefgen, and L. W. Gulrich, *Macromolecules*, **10**, 1390 (1977).

(18) P. W. Morgan, *Macromolecules*, **10**, 1381 (1977).

(19) S. Y. Park, S. W. Lee, and T. J. Oh, *J. Appl. Polym. Sci.*, **102**, 640 (2006).

(20) P. J. Flory, *Proc. R. Soc. Lond. Ser. A*, **234**, 73 (1956).

(21) W. Maier and A. Saupe, *Z. Naturforsch.*, **15a**, 287 (1960).

(22) Y. Eom and B.C. Kim, *Polymer*, **55**, 2570 (2014).

(23) R. Al-Itry, K. Lamnawar, and A. Maazouz, *Polym. Degrad. Stab.*, **97**, 1898 (2012).

(24) C. E. Brunchi, S. Morariu, and M. Bercea, *Colloid Surf. B*, **122**, 512 (2014).

(25) Y. H. Cho, K. S. Dan, and B. C. Kim, *Korea-Aust. Rheol. J.*, **20**, 73 (2008).

(26) W. S. Lyoo, B. C. Kim, and W. S. Ha, *Polym. Eng. Sci.*, **37**, 1259 (1997).

(27) K. M. Digianantonio, S. A. Glover, J. P. Johns, and A. A. Rosser, *Org. Biomol. Chem.*, **9**, 4116 (2011).

(28) V. N. Tsvetkov and I. N. Shtennikova, *Macromolecules*, **11**, 306 (1978).

(29) M. Bercea, S. Morariu, and D. Rusu, *Soft Matter*, **9**, 1244 (2013).

(30) E. K. Chamberlain and M. A. Rao, *Food Hydrocoll.*, **14**, 163 (2000).

(31) P. H. Richardson, J. Willmer, and T. J. Foster, *Food Hydrocoll.*, **12**, 339 (1998).

(32) X. J. Xu, W. Liu, and L. N. Zhang, *Food Hydrocoll.*, **20**, 723 (2006).

(33) D. W. Chae and B. C. Kim, *Compos. Sci. Technol.*, **67**, 1348 (2007).

(34) T. Asada, S. Onogi, and H. Yanase, *Polym. Eng. Sci.*, **24**, 355 (1984).

(35) S. G. Baek, J. J. Magda, and S. Cementwala, *J. Rheol.*, **37**, 935 (1993).

(36) W. R. Burghardt, *Macromol. Chem. Phys.*, **199**, 471 (1998).

(37) W. R. Burghardt and G. G. Fuller, *Macromolecules*, **24**, 2546 (1991).

(38) C. M. Huang, J. J. Magda, and R. G. Larson, *J. Rheol.*, **43**, 31 (1999).

(39) G. Kiss and R. S. Porter, *J. Polym. Sci. Polym. Symp.*, **65**, 193 (1978).

(40) J. J. Magda, S. G. Baek, K. L. Devries, and R. G. Larson, *Macromolecules*, **24**, 4460 (1991).

(41) G. Marrucci, *Macromolecules*, **24**, 4176 (1991).

(42) J. Mewis and P. Moldenaers, *Curr. Opin. Colloid Interface Sci.*, **1**, 466 (1996).

(43) M. Zhou, V. Frydman, and L. Frydman, *J. Phys. Chem.*, **100**, 19280 (1996).