Rheology of polyacrylonitrile-based precursor polymers produced from controlled (RAFT) and conventional polymerization: Its role in solution spinning

J. Kaur, K. Millington, J.Y. Cai

CSIRO Manufacturing, Geelong Technology Precinct, 75 Pigdons Road, Waurn Ponds, Victoria 3216, Australia
Correspondence to: J. Kaur (jasjeet.kaur@csiro.au)

ABSTRACT: Polymer solutions in dimethyl sulfoxide (DMSO) as a solvent, made from reversible addition fragmentation chain transfer (RAFT)-mediated polyacrylonitrile (RAFT¥ PAN) terpolymer with molecular weight (MW) of 260,000 g/mol and dispersity (Đ) of 1.29, behave differently under applied shear stress than polymer solutions made from conventional PAN (Control PAN) with similar MW (258,000 g/mol) but Đ of 2.05 in the same solvent. The unique rheology of RAFT PAN is because of the reduced amount of high MW polymer fractions. Specifically, a 25% (w/v) polymer solution of RAFT PAN had a viscosity of 198 Pas while the equivalent control PAN polymer solution had a viscosity of 968 Pas at a shear rate of $1\ s^{-1}$. Also, RAFT PAN polymer solutions had a longer Newtonian plateau than control PAN polymer solutions. This exhibits more liquid character in RAFT PAN polymer solutions than control PAN polymer solutions at same temperature and concentration. In dynamic tests, RAFT PAN polymer solutions gelled slower than their equivalent control PAN polymer solutions because of their longer polymer chain relaxation times. Slow gelling and higher liquid character in RAFT PAN polymer solutions can result in obtaining stronger and finer precursor fibers during wet spinning. Since RAFT PAN polymer solutions exhibit low viscosity and higher liquid character when compared to its equivalent control PAN at same concentration and temperature, these can allow a wider working window for wet spinning and can also allow higher solid content in the polymer solutions that remain easy to wet spin. This is expected to lead to compact and finer fibers with less voids and higher strength. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44273.

INTRODUCTION

The quality of the precursor fiber has a large impact on carbon fiber quality in terms of its processing performance, production yield, and cost.[1] Polyacrylonitrile (PAN) precursor fiber is used to make high strength carbon fiber commercially due to its high strength, crystallinity, and yield.[2] The precursor fiber quality depends on the characteristics of the polymer it is made from[3–5] and on conditions used for spinning these polymers into precursor fibers.[6–8] A polymer with high molecular weight (HMW) of >250,000 g/mol and low dispersity (Đ) (<1.5) is expected to result in high-quality polymer.[9,10] The spinning variables are required to be chosen carefully for obtaining fiber with high orientation and minimum defects and voids.[11–13]

The ease of spinning (spinnability) of the polymer solutions can be depicted through rheology studies. When a polymer solution passes through narrow holes of the spinneret during wet spinning, it undergoes shear stress. Similarly shear stress can be applied to polymer solutions in a rheometer and changes in their viscosity can be studied.[14] It is essential to find the gelation point of the polymer solutions to prevent them from gelling before spinning and to promote the sol–gel transition in the coagulation bath.[15] Rheology tests can predict the gelation of polymer solutions.[16,17] Using rheology to study the flow characteristics and gelation in polymer solutions before wet spinning is favorable because a small amount of polymer solution is used as a test sample.

The polymer composition,[18] the MW,[19] Đ, the sequence of the various comonomers in the polymer, and the type of the solvent are all important factors that determine the viscosity of polymer solutions. HMW polymers of PAN have been synthesized using conventional free radical polymerization.[20] These HMW polymers have high dispersity index (Đ) of >2. As a result of high Đ, very high MW polymer chains are also present. These high MW polymer chains are difficult to dissolve in an organic solvent. Hence preparing a solution with high polymer content

---

Additional Supporting Information may be found in the online version of this article.

using a HMW polymer is difficult, as these form high viscosity solutions which are difficult to spin. Previous studies have shown that a high Đ shows a similar increase in viscosity as branching in polymer chains.[21,22] In a study on melt spinning of polypropylene, low Đ polymer solutions were easier to spin and resulted in finer fibers.[23] The ease of spinning was estimated from the take up speeds of the spun fibers and not rheology. In another study by Chari et al.,[1] the effect of Đ has been observed on mechanical properties of carbon fiber obtained from many different commercial manufacturers. As these fibers had different MWs, their Đ's cannot be compared.

In our study, we used polymers synthesized using a living/controlled polymerization technique known as reversible addition fragmentation chain transfer (RAFT).[9,24] RAFT can produce polymers with predetermined MW and lower Đ than obtained by conventional free radical polymerization. Design of polymers using RAFT can provide precise control over the viscosity and spinning of polymers into fibers.[25] High MW and low Đ polymers have been successfully synthesized using RAFT.[26,27] RAFT-mediated polymers have also been used to make carbon fibers for research purposes to understand their influence on fiber spinning, precursor fiber, and carbon fiber properties.[26] We hypothesize that using RAFT technique, it is possible to spin solutions with higher polymer content into fibers by wet spinning. These polymer solutions will be easier to spin as their viscosity will be within the range of spinnable viscosity due to reduced amount of much higher MW polymers in the sample which resulted in their low Đ.

In previous literature, rheology of PAN/carbon nanotubes (CNTs) polymer solution in 50% sodium thiocyanate was studied to understand the effect of CNTs on the flow properties of the polymer solution.[28] Rheology of ultra-HMW polymer solution was studied to find the time the polymer solution takes to form crosslinks before reaching the gel point.[15,29] Rheological investigations have also been done to study the effect of nonsolvent (e.g., water) on the polymer solution. Addition of water to the PAN/solvent solution helped to reduce the interaction of polymer and solvent, causing it to gel.[30,31]

This is the first report investigating into the rheology of RAFT-mediated (RAFT PAN) polymer solutions. A systematic study comparing the rheology of polymer solutions made using conventional and RAFT polymerization has been designed. As RAFT polymer has not yet been used commercially to make precursor fibers, an investigation into its rheological properties can give a better picture on their ease of spinning. The viscosity and sol–gel transition of these polymer solutions was tested using steady state and dynamic state rheology, respectively. This methodology will help to identify polymer solutions that can be used to improve the precursor fiber quality.

EXPERIMENTAL

PAN Precursor Polymers
The control and RAFT PAN polymers were prepared by solution polymerization using a 7-L Parr reactor. In a typical polymerization procedure, a mixture of acrylonitrile (AN), comonomers itaconic acid (IA) and methyl acrylate (MA), dimethyl sulfoxide (DMSO), and an initiator 2,2′-

Table I. Feed Concentrations of the Monomers, the MW and Đ of the Control and RAFT PAN

Polymer	AN (wt %)	MA (wt %)	IA (wt %)	M_n (g/mol)	Đ
Control	96.5	2.2	1.3	260,000	2.05
RAFT	96.5	2.2	1.3	258,000	1.29

azobisisobutylonitrile (AIBN) was introduced to the reactor. For the RAFT polymerization, a RAFT agent, 4-cyano-4 phenylcarbanothioylthio pentanoic acid, was also added. The molar ratio of [AN]:[RAFT]:[AIBN] ≈ 22,000:2:1. The reactor was degassed by purging with nitrogen, followed by vacuum application. After degassing, the reactor was filled with nitrogen and sealed. The reactor was gradually heated to 60 °C and held for 20 h. After the polymerization was complete, the polymer was precipitated in methanol, washed with water and methanol, and dried in a vacuum oven. A control polymer was prepared using a conventional free radical polymerization method at 70 °C for 2 h and 15 min.

Table I shows the feed concentrations of the monomers, and the MW and Đ of the control and RAFT PAN obtained. Both control and RAFT PAN produced had similar MW but different Đ. Supporting Information Figure S1 shows the graphs of retention time versus intensity and dispersity distribution of control and RAFT polymers obtained from gel permeation chromatography.
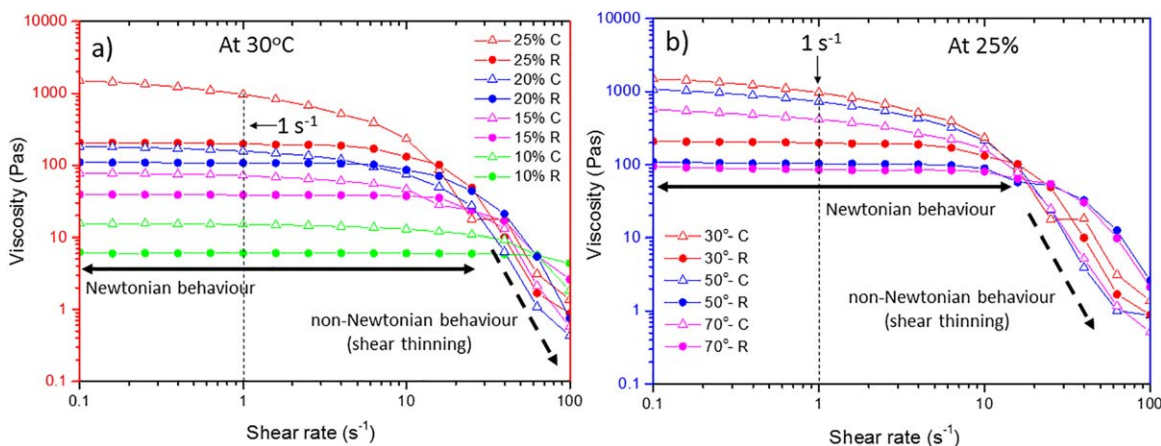
Preparation of Polymer Solution
The control and RAFT PAN were dissolved in DMSO with 99.9% purity from VWR chemicals to prepare weight per volume (w/v) solutions of different concentrations. The concentrations used were 25%, 20%, 15%, and 10%. The solutions were mixed using a laboratory mixer until a homogeneous solution of polymer and solvent was formed at room temperature. Twenty-five percent polymer took longer time (120 h) to dissolve in DMSO when compared to 10% polymer which dissolved in 24 h at room temperature. The solutions were kept at 60 °C in a convection oven for 2 h to get rid of any air bubbles introduced while rolling the solutions on mixer.

Rheology Investigation
A hybrid rheometer (Discovery series) from TA instruments was used to analyze the flow properties and sol–gel transition/gelation/viscoelastic behavior of the polymer solutions. A stainless steel sand blasted 40 mm parallel plate geometry was used for the test. Parallel plate geometry has been used to perform rheology tests in previous studies.[32,33] The gap between the two plates used was 1 mm. Low viscosity silicone oil was used to cover the sample from the sides to prevent evaporation of the solvent during the tests. A new sample was used for each measurement. Each sample was conditioned at 25 °C for 1 min and presheared at 1 s^{-1} for 1 min.[34] The samples were equilibrated for 1 min before testing. Steady state and dynamic state measurements were performed to study the flow and gelation processes, respectively. The experiments were repeated three times.

Steady State Measurements
Shear Sweep Test. A shear sweep test determined the viscosity of the polymer solutions. Viscosity was measured as a function of

Figure 1. Flow sweep tests of control (C) PAN (hollow triangles) and RAFT (R) PAN (solid circles) polymer solutions in DMSO (a) effect of polymer concentration on viscosity at 30 °C and (b) effect of temperature on viscosity at polymer concentration of 25%. [Color figure can be viewed at wileyonlinelibrary.com.]

shear rate at a selected temperature. The temperatures used were 30 °C, 50 °C, and 70 °C. The shear rate range used was 0.1–100 s^{-1}.

Dynamic State Measurements

Oscillation Amplitude. The linear viscoelastic region (LVR) for the polymer solutions at different temperatures can be obtained. In this test, the modulus/viscoelastic behavior was measured as a function of strain. The angular frequency used during the test was 6.28 rad s^{-1}. The range of strain used was 0.1–1000%. The oscillation amplitude was studied at different temperatures of 30 °C, 50 °C, and 70 °C. The samples were kept at the testing conditions for 1 min before testing. Storage modulus (G') determined from the curves represented solid behavior and loss modulus (G'') represented liquid behavior.[35]

Oscillation Frequency. G' and G'' were studied as a function of angular frequency or relaxation time at a fixed strain of 1%. The strain used was in the LVR region. The range of angular frequency was 0.1–600 rad s^{-1}. These curves provide information about the gelation behavior of the polymer solutions.

Oscillation Temperature Sweep. G' and G'' were studied as a function of temperature at a fixed strain and fixed angular frequency. The strain used was 1%. The angular frequency used was 6.28 rad s^{-1}. The rate of heating used was 1 °C/min. The temperature range used was from 5 to 70 °C. These curves inform about the gel points of the polymer solution.

RESULTS AND DISCUSSION

Steady State Tests
Steady state test are used to study flow or resistance to flow (viscosity) in polymer solutions. The flow sweep tests show the effect of shear rate on the viscosity of the polymer solution at a fixed temperature. These tests also depict the Newtonian and non-Newtonian behavior of the polymer solutions.

Most rheological studies have been done on conventional PAN homopolymers,[33,36] copolymers,[14,15,29] and terpolymers[18] in various solvents such as dimethyl formamide (DMF), dimethyl acetamide (DMAc), and ionic liquids.[35,37] These studies have used PAN-based polymers with MWs in the range of 50,000–

150,000 g/mol.[36,38] In our study, a PAN terpolymer of high MW (>250,000 g/mol) was used with DMSO as a solvent. Also, we have shown a comparison of rheology between the conventional PAN-based polymer solutions (control PAN) and RAFT-mediated PAN-based polymer solutions (RAFT PAN).

Figure 1(a) shows the flow sweep tests of control and RAFT PAN polymer solutions in DMSO of different polymer concentrations at 30 °C. It was observed that all samples other than 25% control PAN showed Newtonian behavior (which is, there is no change in viscosity with the increase in shear rate) up to a certain limit as shown by solid arrow in Figure 1(a,b). After the Newtonian plateau, all the samples showed non-Newtonian behavior (which is, the viscosity started to change as shear rate increased further), shown by dashed arrow in Figure 1(a,b). The non-Newtonian behavior was observed to be shear thinning (which is, the viscosity decreased as the shear rate increased further). Shear thinning behavior is favorable for wet spinning process as it prevents the polymer solution from gelling in the narrow holes of the spinneret, and it, therefore, promotes flow. It was also observed that for all samples, low polymer concentration (10%) have longer Newtonian plateau [Figure 1(a,b)].[32] When the polymer concentration is increased from 10 to 25%, a smaller Newtonian plateau was seen. The shear thinning behavior in these highly concentrated solutions of 25% began at much lower shear rates. This also means that high concentration solution is more dependent on shear rate. This is because of the high polymer content of 25% which forms a highly viscous solution. More importantly, in comparison with control PAN, the RAFT PAN polymer solutions have a longer Newtonian plateau, which is extended toward a higher shear rate at all polymer concentrations. Longer Newtonian plateau occurs in RAFT due to reduced amount of very large MW fractions. These result in less-entangled polymer chains.

The effect of polymer concentration on viscosity of solution can also be studied from Figure 1(a). It was seen that under same temperature (30 °C), the viscosity of solution increased with increase in polymer concentration. More importantly, differences were observed between the viscosities of control and RAFT PAN polymer
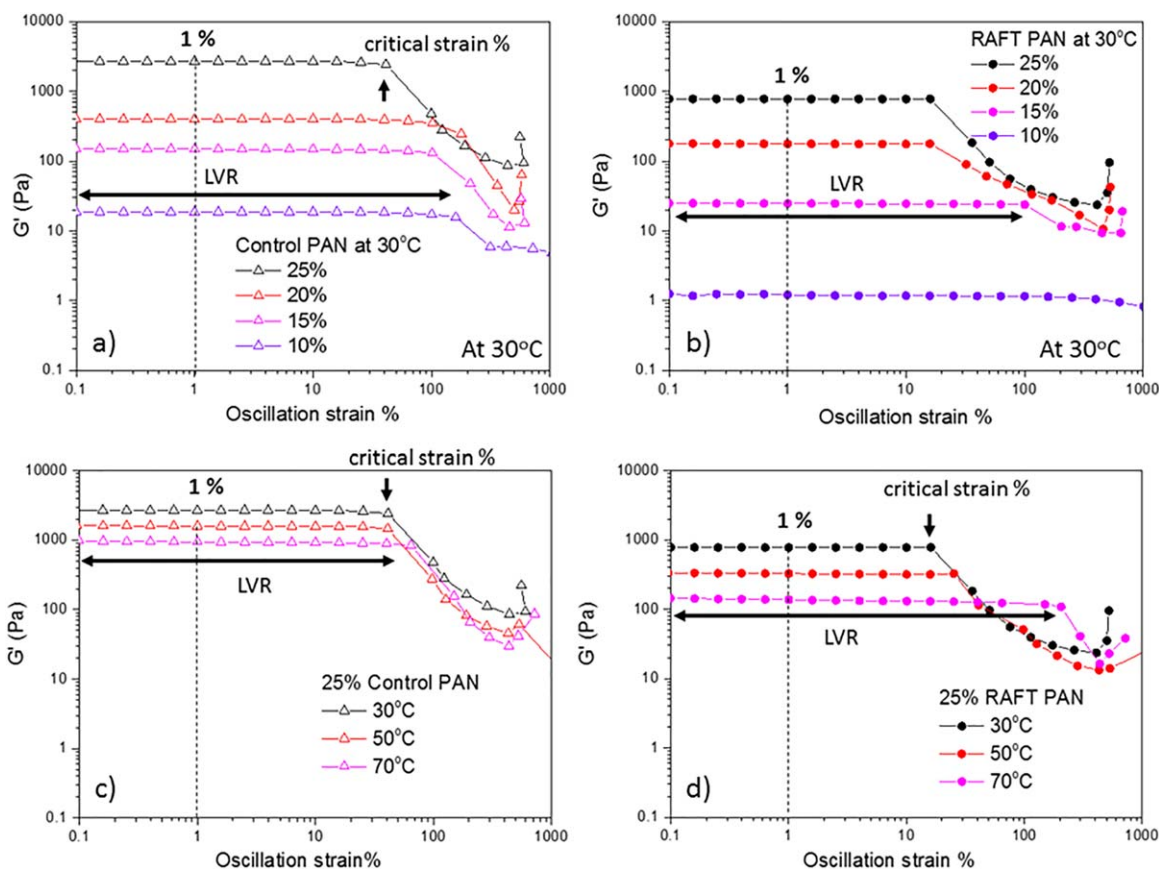
Figure 2. Storage modulus (G')—oscillation strain curves of polymer solutions (a) effect of polymer concentration on G' in control PAN, (b) effect of polymer concentration on G' in RAFT PAN, (c) effect of temperature on G' in control PAN, and (d) effect of temperature on G' in RAFT PAN. [Color figure can be viewed at wileyonlinelibrary.com.]

solutions at same concentration and under same temperature. The viscosity of RAFT PAN polymer solutions was observed to be lower than that of control PAN polymer solutions at same concentration and temperature. This is more important for solutions with high polymer concentration such as 25%. For example; at 25% concentration, RAFT PAN had viscosity of 198 Pas whereas control PAN solutions had viscosity of 968 Pas at 1 s^{-1} shear rate. It can be observed that viscosity can fall out of the spinnable range (which is between 70 and 200 Pas) at 25% concentration for control PAN polymer solutions.[34] This observation informs that 25% RAFT PAN polymer solutions fall within the spinnable viscosity range. Therefore, this depicts that RAFT can offer a broader working window for spinning and can allow high solid content in the solutions which still fall in spinnable range. Such advantages are offered by RAFT due to reduced amount of HMW polymer fractions. The RAFT polymer chains have more homogeneity and are less entangled, which results in lower viscosity.[39] In contrast, the control polymers had high viscosity due to more entangled polymer chains on account of their high Đ. We believe that differences in the viscosities of control and RAFT PAN polymer solutions can be attributed to the different degree of interaction between polymer chains and the DMSO solvent.

Figure 1(b), shows the effect of temperature on viscosity of polymer solutions with 25% concentration. The general trend observed was that, for all samples the viscosity decreased with

increase in temperature. Also, in all samples the Newtonian behavior extended toward higher shear rates at higher temperatures. A similar trend has been observed on PAN-based polymer solutions by Devasia *et al.* previously but in DMF as a solvent.[40] This observation indicated that by heating polymer solution at optimum temperature (at which there is no damage to the polymer), we can achieve viscosity in the desirable spinning range. So, highly concentrated polymer solutions such as 25% can be made to spin when heated.

Dynamic State Rheology

Dynamic state rheology is an important tool to determine any crosslinking and microstructural changes in polymer solutions at low deformation without disrupting the molecular structure.[41] In dynamic tests, a sinusoidal strain is applied to the polymer solution and the output shear stress is also in the form of a sinusoidal wave. Dynamic tests are required to be performed in the LVR, as beyond this region, the materials response no longer remains sinusoidal.[14,37,42] Within LVR, the viscoelastic properties obtained are determined by the material properties as the modulus does not change with the applied strain.

Figure 2 shows storage modulus (G') versus oscillation strain curves of polymer solutions at different concentration under different temperature. In the graphs (a–d), a linear trend is
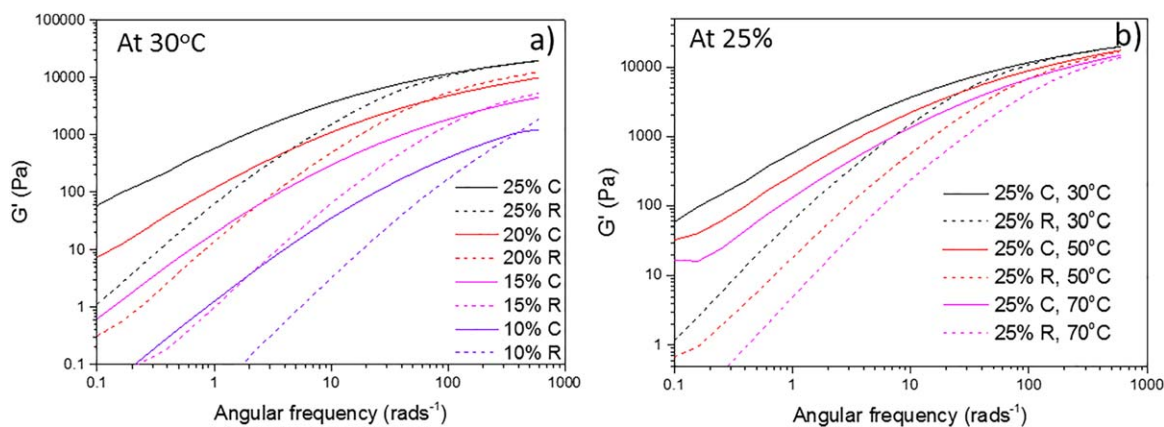
Figure 3. Storage modulus (G')—angular frequency curves of control (C) and RAFT (R) PAN solutions (a) effect of polymer concentration on angular frequency and (b) effect of temperature on angular frequency. [Color figure can be viewed at wileyonlinelibrary.com.]

observed up to a certain strain value, called as critical strain. Below the critical strain, the storage modulus is independent of the oscillation strain. This region is called as the LVR region. Similar results were found by Tan *et al.* for PAN polymer solutions in DMSO.[14] Above the critical strain, the interactive bonds between macromolecules break and the storage modulus decreases sharply.[14] For further experiments, 1% strain was chosen for both control and RAFT PAN polymer solutions as it lies in the middle of the LVR region.

In graphs (a and b), for all samples, LVR increased with decrease in concentration. Another study by Tan *et al.*[32] also showed that the critical strain value shifted to higher value with a decrease in polymer concentration. Also the storage modulus increased with increase in concentration.

More importantly, differences were observed in the LVR of control and RAFT PAN polymer solutions. At polymer concentrations of 10 and 15%, the LVR of RAFT PAN polymer solutions was extended to higher strain than control PAN at same temperature and concentration. Whereas, at polymer concentration of 20% and 25%, the LVR of control PAN was only slightly longer than RAFT PAN polymer solutions. Longer LVR observed in RAFT PAN solutions in comparison with control PAN solutions is due to absence of HMW fractions. Also, low polymer concentrations of 10% and 15% have longer LVR because of less polymer content in them.

In Figure 2(c,d), it can be seen that for all samples, with increase in temperature the storage modulus decreased at same polymer concentration of 25%. The LVR increased with increasing temperature. Under same concentration and temperature, RAFT PAN polymer solutions had lower storage modulus and longer LVR (higher critical strain).

Solid to Liquid Transition. The effect of angular frequency on storage modulus give indication about the solid to liquid transition in polymer solutions. Figure 3 shows the effect of polymer concentration and temperature on storage modulus of the control and RAFT polymer solutions. For all the samples, with the increase in angular frequency, the storage modulus increases and then level off at higher frequency. The point at which

leveling off occurs or when the storage modulus becomes independent of the angular frequency exhibits solid character. The polymer solution below leveling off point is in liquid state. This transition from liquid to solid is because at high frequency the rate of oscillation or input of sine waves exceeds the time scale of molecular rearrangements of the polymer chains.[43]

In Figure 3(a), solid modulus increased with increase in polymer concentration. In Figure 3(b), solid modulus decreased with increase in temperature. More importantly, in Figure 3, the RAFT PAN polymer solutions were more dependent on the angular frequency (deeper slope) than the control PAN polymer solutions at same concentration and same temperature. This meant that RAFT polymer solutions exhibited a higher level of liquid character.

Gelation Behavior. The gelation behavior of the polymer solution was studied in dynamic test mode using storage and loss modulus versus polymer relaxation time curves. Figure 4 shows the storage and loss moduli as a function of polymer chain relaxation time for the 25% control and RAFT PAN polymer solutions in DMSO at 30 °C. The crossover point between the storage and loss moduli indicates the gel point of the polymer solutions. The crossover point for a solution of 25% (w/v) control PAN occurred at a lower relaxation time of 214 s, compared with 235 s for RAFT PAN polymer solution of same concentration [Figure 4(a)]. The lower relaxation time for control PAN polymer solution meant that there was less time for the polymer chains to relax, and therefore they retained their entangled structure[32] and gelled more rapidly. Therefore RAFT PAN polymer solutions appear to have more liquid character due to their higher relaxation time. The relaxation time was higher for polymer solution with 20% polymer content than 25% polymer content. This meant that 20% polymer solution has more liquid character than 25% polymer solution. This is due to less polymer content of 20% when compared to 25%.

More examples can be seen in Table II that shows the comparison of polymer chain relaxation times at the gel-point crossovers for control and RAFT polymers at same concentrations and temperatures. A general trend was observed for both control and RAFT
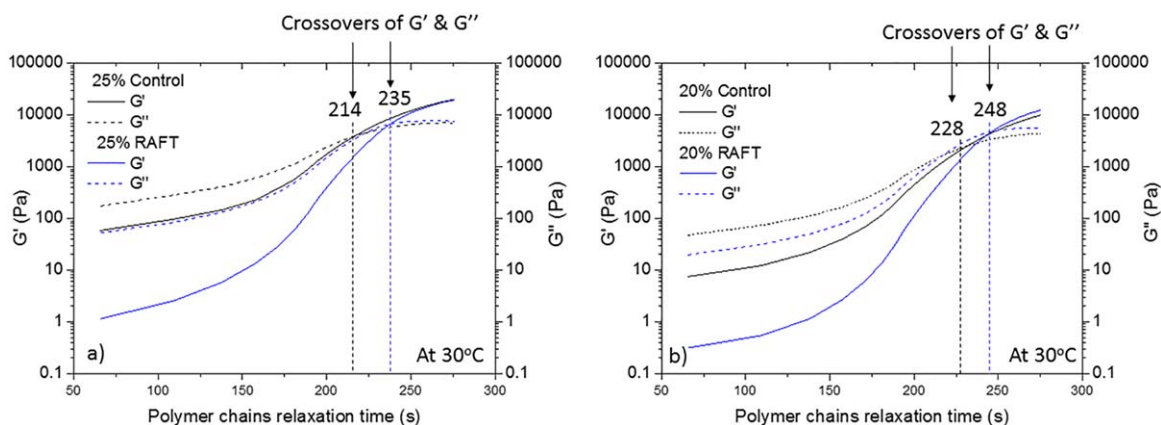
Figure 4. Storage modulus (G') and Loss modulus (G'')—polymer chain relaxation time curves of control and RAFT PAN polymer solutions at 30 °C (a) at 25% polymer concentration and (b) at 20% polymer concentration. [Color figure can be viewed at wileyonlinelibrary.com.]

PAN polymer solutions such as, the polymer chain relaxation time increased with increasing temperature and decreasing polymer concentrations. A similar effect was observed by Brunchi et al.[36] that is higher PAN polymer concentration in DMF showed a crossover gel point at lower relaxation time, which supports our findings. No crossover was seen for polymer solutions with 10% concentration as this concentration was too low to form gel.

It is therefore clear that under same conditions of concentration and temperature, RAFT PAN polymer solutions are more liquid and gel slower than control PAN polymer solutions. This slow gelling will cause the RAFT polymer solutions to be drawn more and produce finer fibers when compared to the control PAN polymer solutions.

Gelation Temperature. Oscillation temperature sweep gives indication about the gelation temperatures of the polymer solutions.[15] The gelation temperature has been measured using dynamic state rheology in previous literature reports.[33,42] This can help to determine the temperature at which the polymer solution should be kept to prevent it from gelling in the spinneret holes. Also, it can be used as a guide to set the temperature of the coagulation bath, which helps gelation of polymer solution into fibers.

Gelation occurs due to crosslinking of polymer chains in a widespread fashion making it unable to flow.[42,44] In polymer solutions, gels can be formed by either increasing the polymer content or by reducing the amount of solvent in solutions.[31]

There are two types of gelation: physical (reversible) and chemical (irreversible). In polymer solutions of PAN, physical gelation occurs due to aggregation that initiates dipole–dipole interactions between the nitrile groups.[41] Physical gelation can easily be achieved by either decreasing the temperature of polymer solution or by allowing the polymer to stand at fixed temperature before spinning so that it can form crosslinks.[31,42] Chemical gelation occurs at higher temperatures (>60 °C) due to chemical bonding/crosslinking.[33]

Figure 5 shows the effect of temperature and polymer concentration on storage and loss modulus. When the temperature was decreased from 70 °C to 5 °C, a crossover between storage modulus and loss modulus was observed for both 25% control and RAFT PAN polymer solutions. The point of crossover between the storage and loss moduli indicates the gelation point temperature. The gelation temperature for polymer solutions with 25% control PAN was 15 °C and for polymer solutions with 25% RAFT PAN was 8 °C. This suggested that RAFT PAN polymer solutions led to gelation at 8 °C lower temperature than control PAN polymer solution. A crossover was observed at 7 °C for polymer solutions with 20% control PAN, but no crossover was observed for 20% RAFT PAN polymer solutions. This is attributed to difference in the Đ of PAN polymers. Since RAFT polymers have reduced amount of HMW polymer fractions, it takes a much lower temperature to form gel when compared to control PAN polymer solutions having high Đ. It was also observed that gelation temperature of a control PAN

Table II. Effect of Polymer Concentration and Temperature on Polymer Chain Relaxation Time of RAFT and Control PAN Polymer Solutions

Variables	Polymer chains relaxation time (s)							
Concentration (%)	25		20		15		10	
Temperature (°C)	Control	RAFT	Control	RAFT	Control	RAFT	Control	RAFT
30	214	235	228	248	249	261	261	268
50	229	248	241	255	254	269	—	—
70	235	254	248	262	261	274	—	—
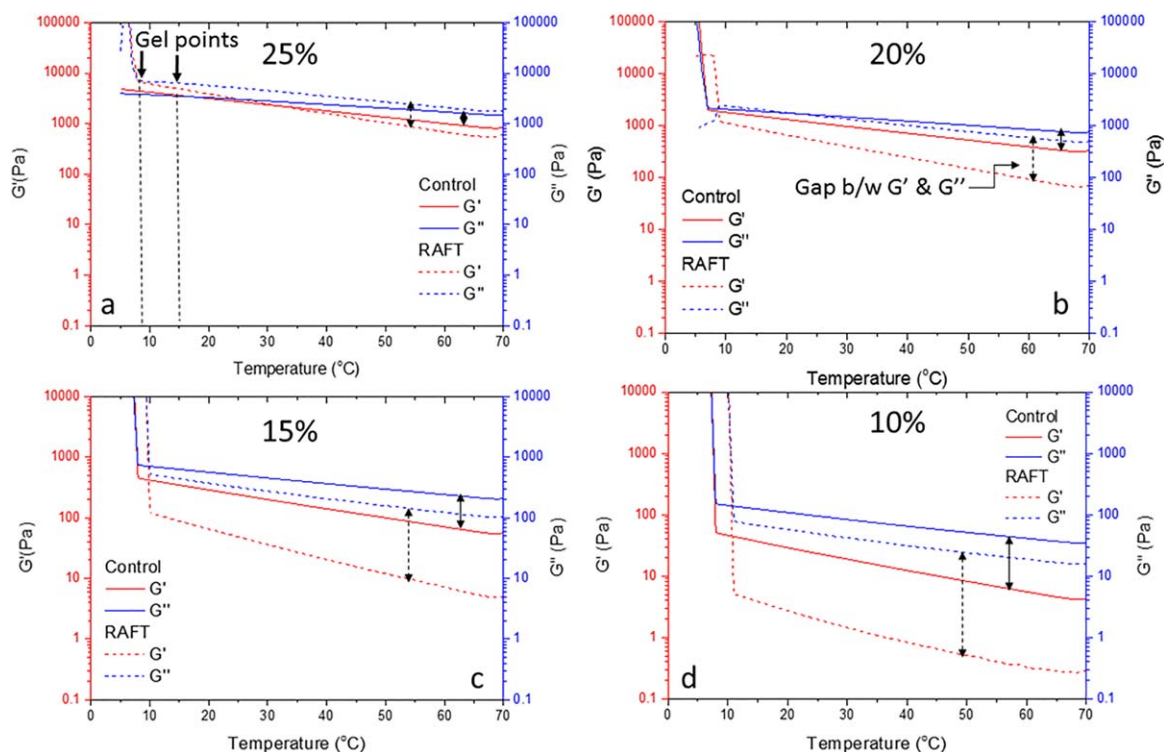
Figure 5. Effect of temperature and polymer concentration on storage (G') and loss modulus (G''). [Color figure can be viewed at wileyonlinelibrary. com.]

solution with 25% polymer content in DMSO was 11 °C higher than that of a control PAN polymer solution with 20% polymer content. In a study by Tan *et al.* previously it was found that the gel point of 23% PAN polymer solution in DMSO was 10 °C higher than 20%.[42] These findings support our result. It was also observed that for the 10% PAN polymer solution, an abrupt increase in modulus was found at 12 °C in control and at 9 °C in RAFT PAN polymer solutions. This is due to the formation of DMSO crystals. The freezing point of DMSO is 18 °C; however, the presence of polymer results in freezing point depression.

The gap between storage and liquid modulus was more in RAFT polymers than in the control polymers (Figure 5). This gap increased with decrease in polymer concentration [Figure 5(d)]. Additionally, the gap between storage and liquid modulus decreased along with the decrease in temperature for both control and RAFT polymers. The behavior of the polymer solution can be either one or two phase with change in temperature. In one phase behavior, the polymer solution either liquid or gel, remains in its existing phase. But if the polymer changes from its liquid phase into gel or vice versa with change in temperature, it is called two phase or divergent behavior. In our study, divergent behavior was exhibited by the polymer solutions as they showed a sol to gel transition with decrease in temperature in 25% and 20% control and RAFT PAN polymer solutions. Therefore, for the polymers used in this study, the polymer solutions should be spun in a low temperature bath to assist the sol–gel transition. Gelation leads to fibers that can be subjected to multistage drawing, and usually one can obtain a high drawing ratio,[17] leading to the production of finer fibers.

CONCLUSIONS

Flow and oscillation tests were done on HMW ($>$250,000 g/ mol) conventional and RAFT-mediated polymer PAN (RAFT PAN) solutions. In flow test, all samples showed shear thinning which is, the viscosity decreased as the shear rate increased. Shear thinning behavior is favorable for wet spinning process as it prevents the polymer solution from gelling in the narrow holes of the spinneret, and therefore, it promotes flow. In comparison with control PAN, the RAFT PAN polymer solutions had a longer Newtonian plateau, which is extended towards a higher shear rate at all polymer concentrations. Longer Newtonian plateau occurred in RAFT due to reduced amount of very large MW polymer fractions. These result in less-entangled polymer chains.

The viscosity of RAFT PAN polymer solutions was observed to be lower than that of control PAN polymer solutions at same concentration and temperature. This was more important for solutions with high polymer concentration such as 25%. At 25% concentration, RAFT PAN had viscosity of 198 Pas whereas control PAN solutions had viscosity of 968 Pas at 1 s^{-1} shear rate. This indicated that 25% RAFT PAN polymer solutions fell within the spinnable viscosity range but equivalent control PAN polymer does not. Therefore, this depicts that RAFT can offer a broader working window for spinning and can allow high solid content in the solutions which still fall in spinnable range. These advantages are offered by RAFT due to reduced amount of HMW polymer fractions. It was also found that by heating polymer solutions at optimum temperature (at which there is

no damage to the polymer), we can achieve viscosity in the desirable spinning range.

In dynamic tests, 1% strain was chosen in the LVR for all samples. For all the samples, with the increase in angular frequency, the storage modulus increased and then leveled off at higher frequency. The point at which leveling off occurs or when the storage modulus becomes independent of the angular frequency exhibits solid character. The polymer solution below leveling off point is in liquid state. The RAFT PAN polymer solutions were more dependent on the angular frequency (deeper slope) than the control PAN polymer solutions at same concentration and same temperature. This meant that RAFT polymer solutions exhibited a higher level of liquid character. It was seen that under same conditions of concentration and temperature, RAFT PAN polymer solutions were more liquid and gelled slower than control PAN polymer solutions. It was also observed that 25% RAFT PAN gelled at 8 °C lower temperature than equivalent control PAN polymer solutions. This meant that RAFT polymer solutions gel slower than control PAN solutions. Slow gelling and higher liquid character in RAFT PAN polymer solutions can result in higher drawing before they coagulate during wet spinning, resulting in finer fibers.

ACKNOWLEDGMENTS

REFERENCES

1. Chari, S.; Bahl, O.; Mathur, R. *Fibre Sci. Technol.* **1981**, *15*, 153.

2. Rahaman, M. S. A.; Ismail, A. F.; Mustafa, A. *Polym. Degrad. Stabil.* **2007**, *92*, 1421.

3. Chen, J.; Wang, C.; Ge, H.; Bai, Y.; Wang, Y. *J. Polym. Res.* **2007**, *14*, 223.

4. Nishihara, Y.; Furutani, Y.; Toramuru, M.; Yasunaga, T.; Toramaru, M. [to Mitsubishi Rayon Co. Ltd. (Mitr-C)]. U.S. Pat. 4902452-A (**1987**).

5. Ju, A.; Guang, S.; Xu, H. *Carbon* **2013**, *54*, 323.

6. Knudsen, J. *Text. Res. J.* **1963**, *33*, 13.

7. Watkins, W. W. (to DuPont). U.S. Pat. 2426719A (**1947**).

8. Masson, J. Acrylic Fiber Technology and Applications; CRC Press, Marcel Dekker Inc., USA, **1995**.

9. Cai, J. Y. U.S. Pat. 20140271442A1 (**2014**).

10. Tang, L.; Thomas, A. D.; Harmon, B. D. U.S. Pat. 20150174807 (**2014**).

11. Rennhofer, H.; Loidl, D.; Puchegger, S.; Peterlik, H. *Carbon* **2010**, *48*, 964.

12. De-Hong, W.; Jun-Jie, H.; Xue-Qing, X.; Guang, M.; Yu, G.; Chun-Xiang, L.; Zhong-Hua, W. *Chin. Phys. C* **2011**, *35*, 870.

13. Liu, H.; Li, G.; Wang, C. *J. Wuhan Univ. Technol. Mater. Sci. Ed.* **2010**, *25*, 200.

14. Tan, L.; Wan, A.; Pan, D. *Polym. Int.* **2011**, *60*, 1047.

15. Du, W.; Chen, H.; Xu, H.; Pan, D.; Pan, N. *J. Polym. Sci. Part B: Polym. Phys.* **2009**, *47*, 1437.

16. Fujiyama, M.; Kondou, M. *J. Appl. Polym. Sci.* **2003**, *90*, 1808.

17. Tan, L.; Liu, S.; Song, K.; Chen, H.; Pan, D. *Polym. Eng. Sci.* **2010**, *50*, 1290.

18. Malkin, A.; Ilyin, S.; Roumyantseva, T.; Kulichikhin, V. *Macromolecules* **2012**, *46*, 257.

19. Devasia, R.; Nair, C.; Ninan, K. *Polym. Adv. Technol.* **2008**, *19*, 1771.

20. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press, Ithaca, United States, **1953**.

21. Hatzikiriakos, S. G. *Polym. Eng. Sci.* **2000**, *40*, 2279.

22. Berry, G. C.; Fox, T. G. The Viscosity of Polymers and Their Concentrated Solutions; Springer: Mellon Institute, Pittsburgh, PA, **1968**.

23. Misra, S.; Lu, F. M.; Spruiell, J.; Richeson, G. *J. Appl. Polym. Sci.* **1995**, *56*, 1761.

24. Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379.

25. Braunecker, W. A.; Matyjaszewski, K. *Progr. Polym. Sci.* **2007**, *32*, 93.

26. Sporl, J. M.; Ota, A.; Beyer, R.; Lehr, T.; Muller, A.; Hermanutz, F.; Buchmeiser, M. R. *J. Polym. Sci. A: Polym. Chem.* **2014**, *52*, 1322.

27. Moskowitz, J. D.; Abel, B. A.; McCormick, C. L.; Wiggins, J. S. *J. Polym. Sci. Part A: Polym. Chem.* **2016**, *54*, 553.

28. Wang, B.; Li, J.; Wang, H.; Jiang, J.; Liu, Y. Rheological Behavior of Spinning Dope of Multiwalled Carbon Nanotube/Polyacrylonitrile Composites, Macromolecular Symposia; Wiley Online Library; Wiley, VCH Weinheim, Germany, **2004**, *216*, 189–194.

29. Tan, L.; Pan, J.; Wan, A. *Colloid Polym. Sci.* **2012**, *290*, 289.

30. Cheng, L.; Ouyang, Q.; Wang, H. J. *J. Macromol. Sci.* **2009**, *48*, 617.

31. Bisschops, J. *J. Polym. Sci.* **1955**, *17*, 89.

32. Tan, L.; Liu, S.; Pan, D.; Pan, N. *Soft Matter* **2009**, *5*, 4297.

33. Brunchi, C. E.; Morariu, S.; Bercea, M. *Rev. Roum. Chim.* **2008**, *53*, 35.

34. Morris, E. A.; Weisenberger, M. C.; Bradley, S. B.; Abdallah, M. G.; Mecham, S. J.; Pisipati, P.; McGrath, J. E. *Polymer* **2014**, *55*, 6471.

35. Liu, W.; Cheng, L.; Zhang, H.; Zhang, Y.; Wang, H.; Yu, M. *Int. J. Mol. Sci.* **2007**, *8*, 180.

36. Brunchi, C. E.; Bercea, M.; Morariu, S. *e-Polymers* **2009**, *9*, 803.

37. Tanaka, Y. Viscoelastic Properties of Polyacrylonitrile Gels: Dependence of Sol-Gel Transition on Concentration and

Aging Time, Macromolecular Symposia; Wiley Online Library; Wiley, VCH Weinheim, Germany, **2003**, *200*, 265–270.

38. Tan, L.; Chen, H.; Pan, D.; Pan, N. *J. Appl. Polym. Sci.* **2008**, *110*, 1997.

39. Qiu, J.; Charleux, B.; Matyjaszewski, K. *Progr. Polym. Sci.* **2001**, *26*, 2083.

40. Devasia, R.; Reghunadhan Nair, C.; Ninan, K. *J. Macromol. Sci. Part A: Pure Appl. Chem.* **2008**, *45*, 248.

41. Bercea, M.; Morariu, S.; Brunchi, C. E. *Int. J. Thermophys.* **2009**, *30*, 1411.

42. Tan, L.; Liu, S.; Pan, D. *J. Phys. Chem. B* **2008**, *113*, 603.

43. Barnes, H. A.; Hutton, J. F.; Walters, K. An Introduction to Rheology; Elsevier, Amsterdam, The Netherlands, **1989**.

44. Kavanagh, G. M.; Ross-Murphy, S. B. *Progr. Polym. Sci.* **1998**, *23*, 533.