Viscoelastic Relaxation and Molecular Mobility of Hyperbranched Poly(ε-caprolactone)s in Their Melt State

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ABSTRACT

The dynamic viscoelastic relaxation behavior and the molecular mobility of a series of hyperbranched poly(ε-caprolactone)s (HPCLs) possessing the molecular architectural variation and their linear counterpart (LPCL), were characterized and evaluated in conjunction with the different lengths of the linear backbone segments, and the different relative degrees of branching (DBs). The relative DBs, determined by the branching ratio values, decreased with increasing the linear backbone lengths. Dynamic viscoelastic relaxation measurements exhibited unentangled behavior for HPCLs compared to the apparently entangled linear, and the parallel $G'(\omega)$ and $G''(\omega)$ curves were observed for the HPCLs, while the LPCL exhibited a typical curve. The molecular mobility of three HPCLs, determined by the correlation time, τ_c, and the activation energy, E_a, was found to be higher than that of LPCL, and was observed to enhance with decreasing lengths of oligo(ε-caprolactone) segments and increasing relative DB.

Keywords: hyperbranched poly(ε-caprolactone), dynamic viscoelastic relaxation, molecular mobility; correlation time, activation energy

1 INTRODUCTION

Recently, the molecular motion in polymers has received considerable attention as a bridge to connect the structure-property relationships since the aspect of molecular behavior is inevitably related to the chemical structure and molecular environment and seems to exert the greatest influence on the relevant physical and mechanical properties in the end use.[1-3] Hyperbranched polymers have been considered to be developed into tailor-made materials with high performance and/or novel functionality at a reasonable cost due to the advantageous synthetic simplicity together with the unique mechanical, rheological, and compatibility properties.[2-6] In order to correlate the specific molecular structure and architecture with the unique properties in hyperbranched polymers, it is prerequisite to elucidate the molecular motion, which is systematically characterizing and explaining the correlation.

In the present paper, hyperbranched poly(ε-caprolactone)s (HPCLs), designed to incorporate the different lengths of the linear homologous oligo(ε-caprolactone) backbone segments consisting of 5, 10, and 20 ε-caprolactone monomer units (thereby referred to as HPCL–5, –10, and –20, respectively), were synthesized, and their dynamic viscoelastic relaxation behavior and the molecular mobility were compared to their linear counterpart (LPCL) whose chemical structure are identical and molecular weights are similar to those of HPCLs. The relative degrees of branching (DBs) for the HPCLs were determined by the branching ratio values calculated from the ratio of mean-square radius of gyration of each HPCL to that of LPCL. The focal point of this study is to elucidate and compare the dynamic viscoelastic relaxation behavior and the molecular mobility of the HPCLs and the LPCL in their melt state in conjunction with the molecular architectural difference which is the different length of the linear backbone segments and the different relative DB.

2 EXPERIMENTAL

2.1 Materials

Hyperbranched poly(ε-caprolactone)s (HPCLs), designed to incorporate the different lengths of the linear homologous oligo(ε-caprolactone) backbone segments consisting of 5, 10, and 20 ε-caprolactone monomer, were synthesized. HPCLs were synthesized according to a reaction developed by Trollsås ea al.[7] linear poly((ε-caprolactone) (LPCL), whose chemical structure and molecular weight is similar to those of the HPCLs, was commercially purchased and used as a linear counterpart to the HPCLs.
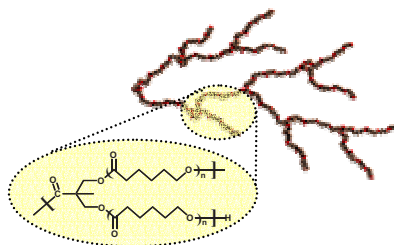

Figure 1: Schematic draw of hyperbranched poly(ε-caprolactone).

2.2 General Characterizations

Measurements of ^{1}H NMR and SEC-MALLS were performed to confirm molecular structures and weights of samples. The radii of gyration of samples were measured by small angle X-ray scattering (SAXS). The melting temperatures were determined by differential scanning calorimetry (TGA).

2.3 Dynamic Viscoelastic Relaxation Measurements

The dynamic viscoelastic relaxation properties of three HPCLs and an LPCL were measured with a Paar Physica UDS-200 mechanical spectrometer. The measurements were performed in dynamic shear oscillatory mode using 25 mm diameter parallel disc geometry with a gap setting of ca. 2 mm. The range of angular frequency was from 0.1 to 100 rad/s and the range of temperature was selected from 55 to 175 ^{o}C for three HPCLs, and 60 to 180 ^{o}C for an LPCL at an interval of 20 ^{o}C. The lowest temperature of the measurements was limited above the melting temperature, i.e., T_m+ 5 ~10 ^{o}C, depending on the samples, in which the slippage between the sample and the disk did not occur. The strain amplitude of 20% was selected to be large enough for accurate torque signals and small enough to keep the material response in the linear region.

3 RESULT AND DISCUSSION

3.1 Synthesis and Characterizations

The HPCLs were prepared to have the intrinsically different lengths of backbone segments by the use of the different AB$_2$ macromonomers, and referred to as HPCL−5, −10, and −20, respectively. Listed data in Table 1 are the general characteristics of three HPCLs and their linear counterpart, LPCL. The molecular weights were not significantly varied among the HPCLs and also similar to that of the LPCL.

Table 1: General characteristics of hyperbranched poly(ε-caprolactone)s and their linear counterpart.

Sample	$<N_{AB2}>^a$	M_n, NMR^b	M_n^{c}	M_w/M_n^{d}
HPCL-5	8.1	11,510	11,800	1.8
HPCL-10	5.1	12,700	12,600	1.6
HPCL-20	3.3	15,100	15,700	1.5
LPCL			10,700	1.4

[a] Average number of the AB$_2$ macromonomer units incorporated in the HPCLs determined by ^{1}H NMR
[b] Number average molecular weights determined by ^{1}H NMR
[c] Obtained from SEC-MALLS

The information about DB of the HPCLs were alternatively characterized through the comparison of the molecular dimensions of hyperbranched molecules against their linear counterpart, taking into consideration the fact that as more highly branched structures are imparted, the molecular dimensions get decreased. The information about DB obtained in this way is a relative value. It is noteworthy that the branching ratio, g, which is the ratio of mean-square radius of gyration given hyperbranched polymer to that of its linear counterpart of the same chemical structure and the analogous molecular weights, provides an alternative means to characterize the branching structure and hence obtain information about relative DB. [8]

$$g = \frac{\left\langle R_g^{\,2} \right\rangle_{branched}}{\left\langle R_g^{\,2} \right\rangle_{linear}} \tag{1}$$

The parameter g is always less than 1 and decreases with the increase in DB because the branched molecules become more compact compared with the less branched molecules or the corresponding linear counterpart of similar molecular weight. The root-mean-square radii $<R^2>^{1/2}$ (equivalently called as radii of gyration R_g) of three HPCLs and an LPCL were determined by SAXS by performing weighted nonlinear, least-square fits to the scattering curves over the accessible q range with the Zimm particle scattering function, $P_{Zimm}(R_g,q)=1/[1+q^2R_g^2/3]$, which was reported to be the most suitable for determining R_g for hyperbranched polymers.[9] Listed in Table 2 are the radii of gyration for all HPCLs and an LPCL and calculated values of branching ratio. The relative DB increased in the order of HPCL-20<HPCL-10<HPCL-5, indicating that the relative DB increased with the decrease in the length of linear oligo(ε-caprolactone) segments in the HPCLs.

Table 2: Radius of gyration and branching ratio of hyperbranched poly(ε-caprolactone)s and their counterpart.

Sample	R_g (nm)^a	g^{b}
HPCL-5	4.57	0.76
HPCL-10	4.77	0.83
HPCL-20	5.18	0.98
LPCL	5.23	1

[a] Determined from SAXS curves fit by Zimm scattering function.
[b] Branching ratio.

3.2 Dynamic Viscoelastic Relaxation Behavior and Molecular Mobility

From the master curves, all HPCLs and the LPCL exhibited the $G''(\omega)$ over $G'(\omega)$ with an increase in both $G'(\omega)$ and $G''(\omega)$ along shear rate within the experimental

temperature range, which is consistent with the terminal flow behavior for a non-entangled polymer. Also observed curve pattern was that the slopes of the logarithmic plots of $G'(\omega)$ versus ω and $G''(\omega)$ versus ω for the LPCL had values near 2 and 1, respectively, which are in good agreement with the recognized fact that $G'(\omega)$ is proportional to ω^2 and $G''(\omega)$ to ω in their terminal flow region.[10, 11] On the other hand, three HPCLs exhibited parallel $G'(\omega)$ and $G''(\omega)$ within the experimental temperature range, even though these polymers were expected to be in their terminal region from the measured temperature range ($T \approx T_m + 5\ ^\circ C - T_m + 125\ ^\circ C$). The parallel $G'(\omega)$ and $G''(\omega)$ have been reported in the previous works on dynamic viscoelastic behaviors of star polymer melts[12] and branched polymer melts having long chain branching and/or short chain branching.[13,14] The junction point of $G'(\omega)$ and $G''(\omega)$, occurring between the rubbery plateau and terminal flow, was observed only in the LPCL in the high frequency limit, while no crossovers were present for all HPCLs within the whole frequency region. (Figure 2)

The dynamic mechanical data must be treated with empirical fitting functions in order to represent the relaxation behavior and determine the single average relaxation time. One of such empirical fitting functions with widespread acceptance is the Havriliak-Negami (H-N) distribution function of relaxation times. The empirical H-N equation is given by [15]

$$G^* = G' + iG'' = G_\infty + \frac{(G_0 - G_\infty)}{[1 + (i\omega\tau_{HN})^\alpha]^\gamma} \qquad (2)$$

with $0 < \alpha, \gamma < 1$ where α is a parameter characterizing a symmetric broadening of the distribution of relaxation times and γ characterizes an asymmetrical broadening. G^* is the complex shear modulus, G_0 and G_∞ are the relaxed and unrelaxed modulus that can be estimated from the values of G' at low- and high-frequency, respectively, and τ_{HN} (τ_c) is the characteristic relaxation time. The correlation times of three HPCLs and an LPCL as a function of temperature are shown in Figure 3. Through the whole range of experimental temperatures, all HPCLs exhibited shorter τ_c values than those of the LPCL, indicating the HPCLs possess faster molecular motion than that of their linear counterpart. Moreover, among three HPCLs, as the length of oligo(ε-caprolactone) segments decreased and as the relative DB increased, the τ_c values decreased, and hence the molecular motion was fastened.

The molecular mobility evaluation are further confirmed by analyzing the apparent activation energy, E_a, determined by a fitting of the τ_{HN}'s to the following Arrhenius equation.[16]

$$\tau_{HN} = \tau_{HN,0} \exp\left(E_{a,\tau_{HN}} / RT\right) \qquad (3)$$

where, $\tau_{HN,0}$ is the pre-exponential factor and R is the gas constant. Recognizing that the apparent activation energy corresponds to the barrier height for the potential hindering motion, the molecular mobility of three HPCLs was higher than that of their linear counterpart. In addition, the molecular mobility of each HPCL was enhanced with the decrease in length of oligo(ε-caprolactone) segments and the increase in the relative DB, which are in good agreement with the τ_{HN} results and can be explained by following aspects. The higher relative DB made the branches in the final HPCLs shorter, and intrinsically shorter branches were incorporated in the final HPCLs by using the AB$_2$ macromonomers having shorter oligo(ε-caprolactone) segments. Therefore, molecular motion in three HPCLs was generated more easily with the lower activation energy because of the existence of more mobile shorter branches, which were comparable to the LPCL possessing no such branched structure.
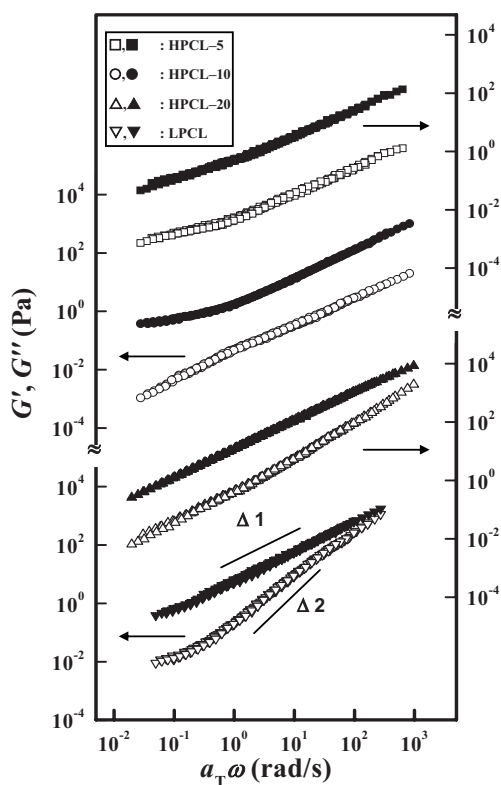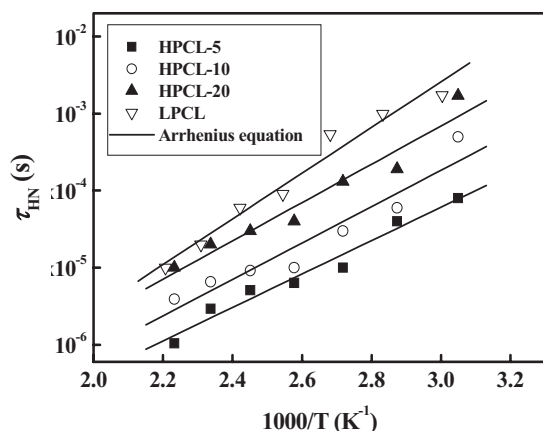

Figure 2: Master curves of the dynamic moduli $G'(\omega)$ (blank) and $G''(\omega)$ (filled), representing the behavior over an extended frequency scale (T_0=115 °C for HPCLs and 120 °C for LPCL). The moduli data were shifted vertically for clarity.

Figure 3: Correlation times, τ_c's, for HPCL–5 (■), HPCL–10 (○), HPCL–20 (▲), and LPCL (▽) as a function of temperature. The solid lines are the fits to the Arrhenius equation.

4 CONCLUSION

In the present paper, three hyperbranched poly(ε-caprolactone)s (HPCL–5, HPCL–10, HPCL–20) were prepared with the structural variation in the backbone chains, which was the different lengths of homologous oligo(ε-caprolactone) segments, and compared with respect to their linear counterpart (LPCL) whose chemical structure and molecular weight were similar to those of the HPCLs.

1. The molecular weights of the resulting HPCLs were not significantly varied. The ratio of mean-square radius of gyration of each HPCL to that of the LPCL, termed as branching ratio, resulted in the relative degree of branching (DB) for individual HPCL, which was found to be considerably influenced by the length of linear oligo(ε-caprolactone) segments; the shorter the oligo(ε-caprolactone) segments, the higher relative DB in the order HPCL–5 > HPCL–10 > HPCL–20.

2. The master curves, where three HPCLs and an LPCL exhibited the $G''(\omega)$ over $G'(\omega)$ with an increase in both $G'(\omega)$ and $G''(\omega)$ along shear rate within the experimental temperature range, indicate terminal flow behavior of non-entangled polymers. The HPCLs exhibited the parallel $G'(\omega)$ and $G''(\omega)$, of which origin is not clear but have been reported for the star polymers and branched molecules, while typical $G'(\omega)$ and $G''(\omega)$ versus ω curve was observed for the LPCL.

3. The correlation time, τ_c, was determined from the dynamic shear loss moduli and the empirical Havriliak-Negami (HN) equation, which provided a unique means to evaluate the molecular mobility. From the τ_c measurements, it was concluded that the molecular mobility of the HPCLs was higher than that of their linear counterpart, LPCL, and was enhanced with the increase in the relative DB of the HPCLs through the entire range of experimental temperatures.

4. From the curve fittings of the correlation times with the Arrhenius equation, novel information about the temperature-dependence of the molecular mobility and the apparent activation energy were provided. The lower apparent activation energy was resulted for the hyperbranched molecules compared to that of their linear counterpart, and the activation energy of HPCLs was decreased with increasing relative DB, indicating the higher molecular mobility and hence the easier molecular motion in the HPCL molecules as the hyperbranched structures were endowed with the shorter intrinsic branches and with the increase in the relative DB.

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