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Toward understanding the effect of substitutes and solvents on entropic and enthalpic elasticity of single dendronized copolymers

Weiqing Shi [a,b], Yiheng Zhang [a], Chuanjun Liu [a,b], Zhiqiang Wang [a], Xi Zhang [a,*], Yanhong Zhang [c], Yongming Chen [c,*]

[a] *Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China*
[b] *Key Lab of Supramolecular Structure and Material, Department of Chemistry, Jilin University, Changchun 130012, People's Republic of China*
[c] *State Key Lab of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*

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Abstract

Using single molecule force spectroscopy (SMFS), we have investigated the single chain elasticity of a series of dendronized copolymers, whose original backbone is styryl dendron and maleic anhydride. The amilysis reaction of maleic anhydride introduces amide and carboxyl side groups. Hence, the copolymer bears three type side groups, Fréchet type dendrons, amides and carboxyls. The single chain elasticity of the polymers in tetrahydrofuran (THF) and chloroform ($CHCl_3$) has been obtained, respectively. There is no hysteresis between the stretching and relaxing force curves of individual polymer chain, indicating that the elongation is carried out at the equilibrium condition. The force curves can be fitted well by the modified freely jointed chain model, which suggests that the elongation of the polymer chain is controlled by the entropic elasticity in the low-force region but dominated by enthalpic elasticity in the high-force region. The polymer with first-generation dendrons shows different elasticities in the two solvents, which should result from the different hydrogen bonds of the dendronized copolymer in two solvents. When the dendron groups are changed to be second and third generations, the single chain elasticity of the polymers is the same in two solvents. Hence, the elasticity of the polymer chain can be different depending on the properties of side groups and solvents.

Keywords: Single molecule force spectroscopy; Single chain elasticity; Dendronized polymer

1. Introduction

Recently, dendronized polymers, a kind of novel dendrimers, has attracted considerable research interest because of their unique molecular architecture and unusual properties [1–7]. The dendronized polymers are polymers uniformly grafted with dendritic wedges. Owing to the steric hindrance, the backbones are extended and they tend to show cylindrical shape as the polymer backbones encapsulated into the dendronized envelope. In contrast to the conventional polymers, the diameter of the dendronized polymers is in the order of a few nanometers rather than a few angstroms [1–7]. Thus, this kind of polymer is regarded as a new type of nanomaterial. The syntheses and properties of many kinds of dendronized polymers have been well documented by Schlüter, Percec and Frey, etc. in recent reviews [1–7]. One of the synthetic approaches is so-called macromonomer approach, which refers to homopolymerization of the dendritic macromonomer through selected polymerization techniques. The advantage of this approach is that the uniform structures of the resulting polymers can be guaranteed since every repeat unit bears one dendron. However, it is difficult to gain the polymers with higher degree of polymerization (DP), because the higher generation the dendritic monomers have, the stronger the steric hindrance is. We have synthesized novel reactive dendronized copolymers through the radical copolymerization of maleic anhydride and styryl-type macromonomers carrying Fréchet type polyether dendrons of the first, second and third generation [8]. The copolymers with rather high molecular weights were obtained even for the third generation monomer under mild conditions. Through the amidolysis reaction, the reactive anhydride groups were easily replaced by the amide and carboxyl groups. Hence, the dendronized polymer bears not only the large-size dendrons but also the two kinds of small side groups along the backbone. Herein, we attempt to study

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* Corresponding authors. Tel.: +86 10 62796283; fax: +86 10 62771149.
E-mail addresses: xi@mail.tsinghua.edu.cn (X. Zhang), ymchen@iccas.ac.cn (Y. Chen).

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the nanomechanics of this kind of dendronized copolymers using atomic force spectroscopy (AFM) based SMFS.

With the high resolution and high sensitivity to measure force signal, SMFS technique is one of the available method to study and manipulate single polymer chains as well as supramolecular systems [9]. Based on the force–extension curves we can obtain the elastic information of the single polymer chain directly [10–18]. Moreover, various information can also be revealed from the force–extension curves, such as the chair-boat conformational transition of individual glucopyranose rings, [19–27] the unfolding process of the helical structure, [28–32] the mechanic energy of the single-molecule photomechanical cycle of azo-polymers, [33] the interfacial conformation and the detachment properties when the polymer chains adsorb on substrates, [34–40] and the interacting strength between the host and guest molecules [41]. Our present research concentrates on revealing the single chain elasticity of one series of dendronized copolymers. The dendronized copolymers are bearing the same amide, carboxyl side groups and the first, second or third generation Fréchet type dendrons, (in brief, G*n*MA-*g*-BA, *n* is the generation of the dendron), whose chemical structures are shown in Chart 1. In general, the polarity of amide and carboxyl is not the same as that of the Fréchet type dendron, which induces the different interaction among the side groups of G*n*MA-*g*-BA and organic solvent molecules. Hence, the factors influencing the elastic property of the polymer single chain seem to become two aspects: the interaction of the side groups and solvent, and the bulky effect of dendron side groups. We expect to clarify the single chain elasticity of G*n*MA-*g*-BA influenced by the two factors.

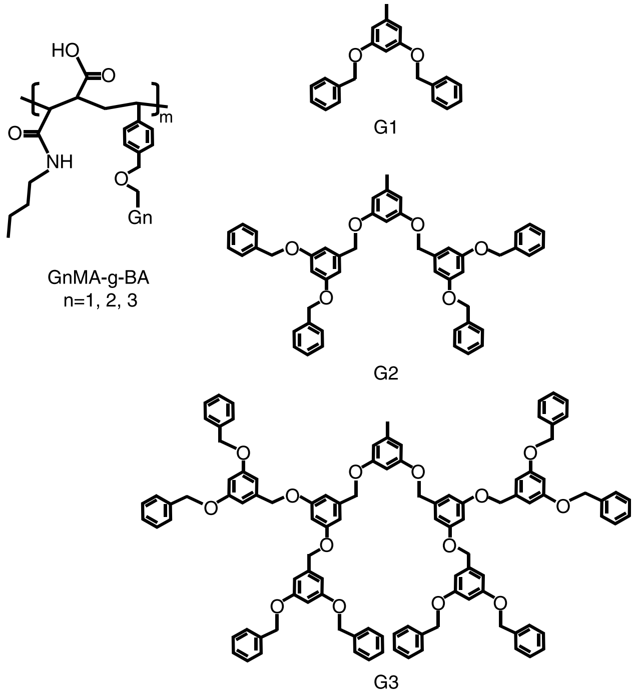

Chart 1. Chemical structures of *Gn*MA-*g*-BA.

2. Experimental section

The syntheses of dendronized alternating copolymers G*n*MA and G*n*MA-*g*-BA were reported elsewhere [8]. G*n* denotes dendron of generation *n*, MA stands for maleic anhydride unit and BA stands for *n*-butylamine. The properties of the dendronized copolymer G*n*MA used in this article are listed in Table 1. The polymers G*n*MA-*g*-BA were the amidolysis products of corresponding G*n*MA, and the amidolysis reaction proceeded completely as confirmed by FT-IR. In the SMFS experiments, the G*n*MA-*g*-BA polymers were dissolved in $CHCl_3$ and the concentrations of the polymer solutions were all approximately 0.5 mg/L.

The quartz slides used as adsorption substrate for the polymers are cleaned as follows: the quartz slides are treated with a hot piranha solution (concentrated H_2SO_4/98%, H_2O_2/30%, 7/3, v/v) for 30 min, then rinsed thoroughly with deionized water (DI water), and finally dried in an oven. About 0.15 mL of each polymer solution was dropped on cleaned quartz slides. After the solution volatilized spontaneously, the slides were used in the SMFS experiment. But for G3MA-*g*-BA, the cleaned quartz slides were coated with G3MA-*g*-BA solution by the spin-coating method (4000 rpm, 30 s).

The force–extension curves (force curves) have been measured at room temperature by molecular force probe 3D (Asylum Research, Santa Barbara, CA). AFM cantilevers used in experiments were commercially available V-shaped Si_3N_4 cantilevers (Veeco, Santa Barbara, CA) with a spring constant ranging of 0.010–0.050 N/m. Force curve measurements were made more than 500 times at different positions of the substrate for each tip/substrate pair. The stretching velocity that means the piezo approach and retraction velocity imposed during the force measurements was about 700 nm/s, if not specified. The details of SMFS experiments have been described elsewhere [11,19,28]. In brief, the polymer is physisorbed on the substrate, then a drop of THF or $CHCl_3$ was placed onto the substrate, and mounted between the cantilever holder and the substrate. When the substrate contacts with the AFM tip by the movement of the *Z*-axis piezo, the polymers will adsorb onto the tip and form the so-called polymer bridge between the tip and the substrate. The polymer bridge will be elongated while the tip and the substrate separate, and the cantilever will deflect by the elastic force. The

Table 1
Properties of the dendronized copolymer G*n*MA ($n=1,2,3$)

Sample	$M_w/M_{n(SEC)}$ [a]	$M_{w(SLS)}$ (g/mol)	M_w r.u.[b] (g/mol)	DP_w [c]
G1MA	1.30	338,100	534.60	535
G2MA	1.18	668,100	959.09	697
G3MA	1.28	880,500	1808.06	487

[a] Size exclusion chromatography (SEC).

[b] Molecular weight (M_w) of repeat unit (r.u.) (taking one pair of dendritic monomer and one succinic anhydride as one repeating unit).

[c] Degree of polymerization calculated from the M_w determined by static light scattering (SLS) measurements.

deflection–extension curves were recorded and converted to force–extension curves [3b].

3. Results and discussion

3.1. Single chain elasticity of G1MA-g-BA

Typical force curves of G1MA-*g*-BA in THF obtained with different tips in different SMFS experiments are shown in Fig. 1. The polymer chains are elongated under the external force. Hence, the length of the polymer chain increases with the increase of the force. Till the polymer ruptures from the weakest point, the force suddenly decreases to zero. The force curves have different contour lengths. This phenomenon is understandable because the molecular weight of polymer is polydisperse and the anchoring point of the AFM tip on the polymer chain is not fixed. In order to compare, the force curves with different contour lengths, we normalized the force curves. Measuring the extension of the polymer chains under the same force value (350 pN), then we divided the force curves with corresponding extension, and obtained the normalized force curves, as superimposed in the inset of Fig. 1. The good superposition proves that the force curves originate from the same elasticity of polymer chains.

Keeping the external force lower than the rupture force, we can repeatedly manipulate the polymer chain stretching and relaxing between the AFM tip and the substrate. Then we can obtain the trace and retrace force curves, both of which are with force signals. The force curve pairs during stretching and relaxing can superimpose well, as shown in Fig. 2. The elasticity of the polymer chain has no hysteresis during the repeated stretching and relaxing processes, which indicates that the elongation of the polymer chains is carried out in an equilibrium state and the force curves manifest the elastic property of single polymer chain.

In a freely jointed chain model (FJC model), which is a classical model for the single polymer chain based on Langevin function, a single polymer chain is treated as an aggregate of many independent segments. The segments are freely jointed, i.e. there is no restriction to their spatial distribution. So each segment can point in every direction with equal probability. If the deformation of the segment under stress is considered, the model can be transformed into a modified freely jointed chain model (in brief, M-FJC model), which is based on the extended Langevin function shown as below.

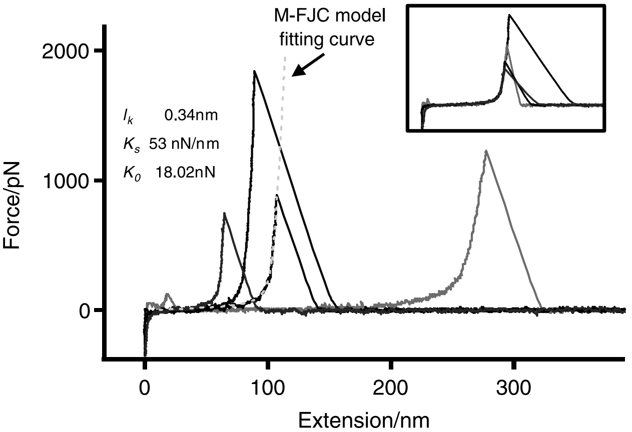

Fig. 1. Typical force curves of G1MA-*g*-BA in THF. The dashed line is the M-FJC model fitting curve. The inset is the force curves after normalization.

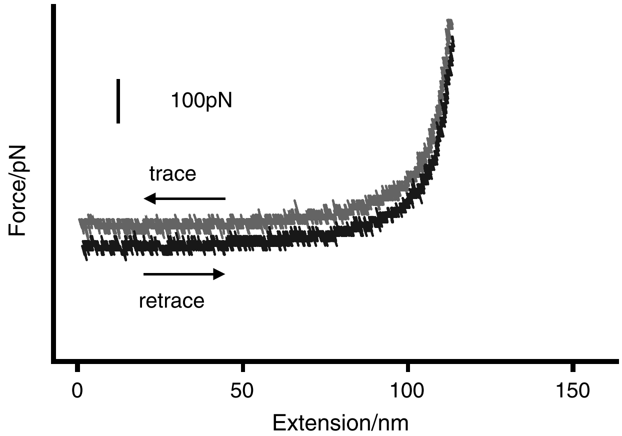

Fig. 2. Successive manipulation of G1MA-*g*-BA single chain in THF. The trace curve is shifted a little in order to be seen clearly. The trace and retrace force curves can superimpose well.

$$x(F) = \left[\coth\left(\frac{Fl_k}{k_BT}\right) - \frac{k_BT}{Fl_k}\right]\left(L_c + \frac{nF}{K_s}\right)$$

In the equation, x represents the extension of a polymer chain (end-to-end distance; in SMFS experiments, x is the section of the polymer chain spanning between the substrate and the AFM tip.); F is the applied force upon an individual polymer chain; L_c is the contour length of the polymer chain; Kuhn length (l_k) is the length of the statistically independent segment; n is the number of segments being stretched in SMFS experiments, which equals to L_c/l_k; k_B is the Boltzmann constant; and T is the Kelvin temperature. The deformability of segments is characterized by the segment elasticity, K_s. The product of the segment elasticity multiplied by the Kuhn length, K_0, represents the normalized segment elasticity of an individual polymer chain. The elasticity of single polymer chain is controlled by both entropy and enthalpy. In the low-force region, the elasticity is mainly contributed by entropy, which reflects the conformation change of the polymer chain, so-called entropic elasticity. However, in the high-force region, the elasticity is governed mainly by enthalpy, which originates from the torsion and rotation of the segments, so-called enthalpic elasticity.

One typical force curve of G1MA-*g*-BA in THF is fitted by an M-FJC model curve, as shown in Fig. 1. Actually, all the force curves can be fitted well by the M-FJC model and the set of fitting parameters is $l_k = 0.34 \pm 0.01$ nm, $K_s = 53.0 \pm 1.0$ nN/nm and $K_0 = 18.02$ nN, though the contour lengths are different. The parameters show a narrow distribution, which further indicates the elastic property of single G1MA-*g*-BA chain in THF solvent.

Similarly, we have performed single chain experiment on G1MA-*g*-BA in $CHCl_3$. The typical force curves of G1MA-*g*-BA with various contour lengths are obtained with different tips in different SMFS experiments. The normalized force curves can superimpose well, which show the same elasticity of G1MA-*g*-BA in $CHCl_3$. Controlling the external force below the rupture force, we obtained the stretching and relaxing force curve pairs of G1MA-*g*-BA in $CHCl_3$. The elasticities during the stretching and relaxing processes are the same, which indicates the equilibrium state of the single chain elongation. The fitting process of the force curves with M-FJC model provides a set of parameters with narrow distribution for the elasticity of G1MA-*g*-BA in $CHCl_3$, as shown in Fig. 3(A): $l_k = 0.34 \pm 0.01$ nm, $K_s = 109.0 \pm 1.0$ nN/nm and $K_0 = 37.06$ nN, which is another proof for the single chain elongation of the polymer. Based on the above experiments, we conclude that the force curves we obtained show the single chain elasticity of G1MA-*g*-BA in $CHCl_3$.

Comparing the normalized force curves of G1MA-*g*-BA in different solvents, as shown in Fig. 3(A), we can see clearly that the force curves superimpose well in the low-force region, but branch in the high-force region. While the elongation of the individual polymer chain is in the initial stage, the superposition of the two force curves indicates that the polymer chains have similar entropic elasticity in THF and $CHCl_3$. When the elongation of the polymer chain continues, the single polymer chain shows different enthalpic change. This elastic difference can be seen markedly from the parameters of K_0 in the two solvents: in THF, K_0 of G1MA-*g*-BA is 18.02 nN; but in $CHCl_3$, K_0 is 37.06 nN. This difference could be related to the change of intramolecular hydrogen bonds of G1MA-*g*-BA in two solvents. As observed by FTIR of G1MA-*g*-BA, vibration band of amide group appeared at around 3014 cm^{-1} in THF and this band shifted to around 3035 cm^{-1} in $CHCl_3$. These data suggested that $CHCl_3$ is more favorable for the formation of intramolecular hydrogen bonds than THF, which could be responsible for the different K_0 of G1MA-*g*-BA in two solvents.

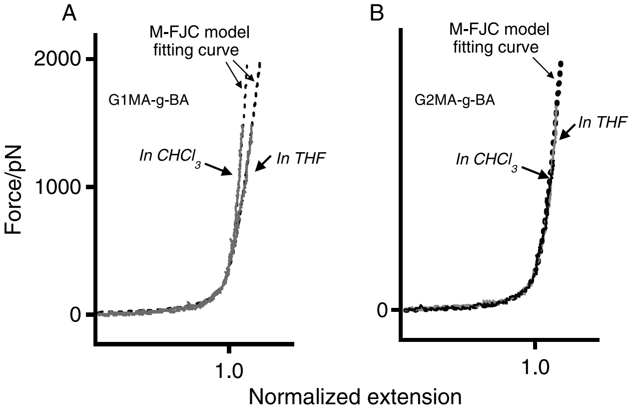

Fig. 3. The normalized force curves of G1MA-*g*-BA and G2MA-*g*-BA in the two solvents, THF and $CHCl_3$. (A) The comparison of G1MA-*g*-BA force curves in different solvents. (B) The comparison of G2MA-*g*-BA force curves in different solvents. The dashed lines are the M-FJC model fitting curves.

3.2. *Elastic comparison of* G*n*MA-*g*-BA *bearing different generations of dendrons*

It is proved that there exists a substitute effect on single chain mechanics in some polymer systems [14,16]. We are wondering if the effect also exists for G*n*MA-*g*-BA bearing different generations of dendrons. For this purpose, we studied the single chain mechanics of G2MA-*g*-BA polymer and compared its elastic property with G1MA-*g*-BA.

With the similar process of G1MA-*g*-BA experiments, we performed the SMFS experiments of G2MA-*g*-BA polymer in THF. The typical force curves of G2MA-*g*-BA polymer in THF were obtained with different tips in different experiments. The force curves with different contour lengths can be superimposed well after normalization. The stretching and relaxing force curve pairs show the same elasticity. The fitting curves of M-FJC model give the parameters of the polymer: $l_k = 0.31 \pm 0.01$ nm, $K_s = 85.0 \pm 1.0$ nN/nm and $K_0 = 26.35$ nN. The distributions of the parameters are narrow. One of the normalized force curves is shown in Fig. 3(B).

Comparing with the normalized force curve of G1MA-*g*-BA in THF, as shown in Fig. 4, the force curve of G2MA-*g*-BA shows higher elasticity in the high-force region than that of G1MA-*g*-BA. In view of the structure difference of these two polymers, we may draw a conclusion that the higher elasticity of G2MA-*g*-BA is probably due to that the dendron side group of G2MA-*g*-BA is larger than that of G1MA-*g*-BA. Hence, the substitute size effect on the single chain elasticity of polymers exists in this series of dendronized polymers.

In $CHCl_3$, the single chain elongation force curves of G2MA-*g*-BA are also obtained successfully. The force curves obtained with different tips in different experiments can superimpose well after being normalized. The stretching and relaxing force curve pairs show the same elasticity. The M-FJC model fits the force curves with a set of narrow distributed parameters. The parameters of the force curves are $l_k = 0.31 \pm 0.01$ nm, $K_s = 85.0 \pm 1.0$ nN/nm and $K_0 = 26.35$ nN. One of the typical normalized force curves is shown in Fig. 3(B). Interestingly, in contrast to the different elasticity of G1MA-*g*-BA in the two solvents, the elasticity of G2MA-*g*-BA in

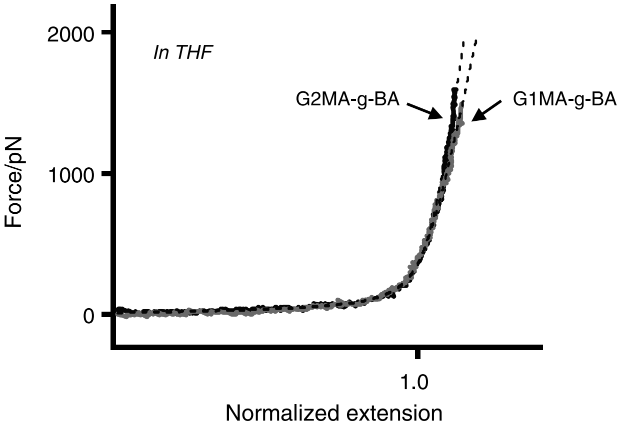

Fig. 4. The comparison of the normalized force curves between G1MA-*g*-BA and G2MA-*g*-BA in THF. The dashed lines are the M-FJC model fitting curves.

Table 2
The M-FJC model parameters of the three polymers

Sample	In THF			In $CHCl_3$		
	l_k (nm)	K_s (nN/nm)	K_0 (nN)	l_k (nm)	K_s (nN/nm)	K_0 (nN)
G1MA-*g*-BA	0.34	53.0	18.02	0.34	109.0	37.06
G2MA-*g*-BA	0.31	85.0	26.35	0.31	85.0	26.35
G3MA-*g*-BA	0.31	85.0	26.35	0.31	85.0	26.35

$CHCl_3$ is the same as in THF, as shown in Fig. 3(B). The same elasticity of G2MA-*g*-BA in different solvents suggests that the larger dendron groups in G2MA-*g*-BA polymer chain become the dominant factor in determining the elasticity of the single polymer chain.

Along the same line of research, we studied the single chain mechanics of G3MA-*g*-BA bearing third generation of dendron side groups and expected it should have similar property as G2MA-*g*-BA. The SMFS experiments of G3MA-*g*-BA polymer were carried out in THF and $CHCl_3$, respectively. The normalized force curves of G3MA-*g*-BA are superimposed well. The stretching–relaxing force curve pairs still show a stretching equilibrium of G3MA-*g*-BA polymer chain. The fitting curves by M-FJC model were carried out and the parameters of the polymer in the two solvents are summarized in Table 2. From these parameters, the elasticities of G3MA-*g*-BA in two solvents are the same. Moreover, as shown in Fig. 5(A), the normalized force curves of G3MA-*g*-BA in two solvents are superimposed well. The same elastic property indicates that the third-generation dendron groups also dominate the single chain elasticity of G3MA-*g*-BA. Interestingly, the elasticity of G3MA-*g*-BA is the same as that of G2MA-*g*-BA in the two solvents, as shown in Fig. 5(B). We are not so clear why G2MA-*g*-BA and G3MA-*g*-BA have shown almost the same K_0 in two solvents, though we speculate that this should be due to the collective effect of different interactions. In addition, with the increase of the generations, the bulky substitutes may not facilitate the formation of intramolecular hydrogen bonds in the dendronized copolymers, which could be the reason that K_0 of G2MA-*g*-BA and G3MA-*g*-BA are even lower than that of G1MA-*g*-BA in $CHCl_3$.

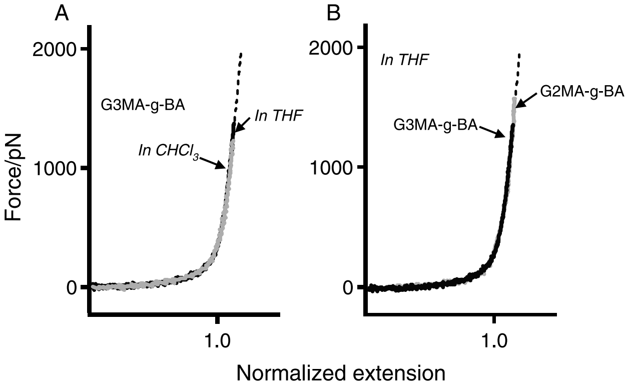

Fig. 5. (A) The typical normalized force curves of G3MA-*g*-BA in THF and $CHCl_3$. (B) The comparison of the force curves of G2MA-*g*-BA and G3MA-*g*-BA in THF. The dashed lines are the M-FJC model fitting curves.

4. Conclusions

Using SMFS technique, we have investigated the single chain elasticity of a series of dendronized copolymers, G*n*MA-*g*-BA. The polymer with first-generation dendrons shows different elasticities in THF and $CHCl_3$, which should result from the different hydrogen bonds of the dendronized copolymer in two solvents. However, the single chain elasticity of G2MA-*g*-BA is larger than that of G1MA-*g*-BA in THF, because of the bulky effect of the side group. Interestingly, G2MA-*g*-BA has shown almost the same single chain elasticity as G3MA-*g*-BA in two solvents. Therefore, the single chain elasticity of these dendronized copolymers can be different depending on the properties of side groups and solvents.

Acknowledgements

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