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Polymer 43 (2002) 1969–1972

polymer

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Polymer Communication

Thermal properties and crystallization behavior of dendritic polyetheramides

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Received 13 August 2001; received in revised form 30 October 2001; accepted 8 November 2001

Abstract

The semi-crystalline dendritic polymers were prepared from the dendritic polyetheramide with hydroxyl end-groups by being grafted with myristoyl chloride, palmitoyl chloride, and octadecyl isocyanate in different substitution degrees, respectively. The thermal properties and the crystallization behavior of the resulted samples were studied by differential scanning calorimetry and optical microscopy, respectively. The experimental results have shown that the length of the alkyl chain attached and substitution degree have apparent influences on the glass transition temperature, melting enthalpy and the size of crystallite. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dendritic polyetheramide; Thermal properties; Semi-crystallization behavior

Polymers with a dendritic backbone, i.e. dendrimers and hyperbranched polymers have obtained increasing attention during the last decade because of their unique characteristics and properties [1]. Both dendrimers, perfectly branched macromolecules and randomly branched hyperbranched polymers are usually amorphous due to their highly branched structures [2]. However, semi-crystallization may be obtained by the attachment of long alkyl chains to the cascade-branched molecular scaffold [3]. Meijer et al. have described that the poly(propylene imine) dendrimers grafted with palmitoyl chloride formed layered bulk structures with the branched cores being expelled from crystalline domains [4]. Hult et al. have observed crystallization behavior of hyperbranched aliphatic polyesters bearing alkyl chains with more than 12 carbons attached to the hyperbranched scaffold [3]. Frey et al. have systematically studied the thermal properties of esterified aliphatic hyperbranched polyether polyols [5].

The glass transition temperature (T_g) is an important parameter for a dendritic polymer with respect to potential applications, e.g. for powder coatings or as a rheology modifier. Several authors have studied the influence of derivatization of dendritic polymers on their T_g [3,6–8].

In the previous paper, we have described the synthesis of dendritic polyetheramide with theoretically 12-hydroxyl end-groups (DPEA-OH) [9]. In this work, a given amount of myristoyl chloride (MC), palmitoyl chloride (PC) and octadecyl isocyanate (OI) dissolved in dichloromethane, triethylamine, anhydrous acetone, respectively, reacted with DPEA-OH in DMF 50 °C until the disappearance of the IR absorption peak at 3380 cm^{-1} for hydroxyl group or 2250 cm^{-1} for isocyanate group of the reaction mixture. The reaction mixture was filtrated, then washed with distilled water and acetone, and finally dried in a vacuum system giving white powder products, which are assigned to DPEA-OH, DPEA-C14, DPEA-C16 and DPEA-C18, respectively. The schematical outlines of those polymers are shown in Fig. 1. The substitution degree of hydroxyl groups grafted by long alkyl chain was calculated from ^1H NMR spectra measured by DMX-500, using the signal intensities of DPEA-OH scaffold and the signal intensities of the substituents. The ^1H NMR spectrum of DPEA-C16 as an example is given in Fig. 2. The methyl protons at long carbon chain ends can be assigned at 0.88 ppm for DPEA-C16. The methylene protons attached to amide group show signals at 2.4 ppm. Using the intensities of these two signals, 89% was obtained as the substitution degree of DPEA-C16. Experimental results from ^1H NMR measurements are listed in Table 1. The substituted samples with MC and PC and about 90% of substitution degree are assigned to DPEA-$C14_{0.9}$ and DPEA-$C16_{0.9}$, respectively, while those with OI and substitution degree of 29, 58 and 87% are assigned to

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PII: S0032-3861(01)00763-7

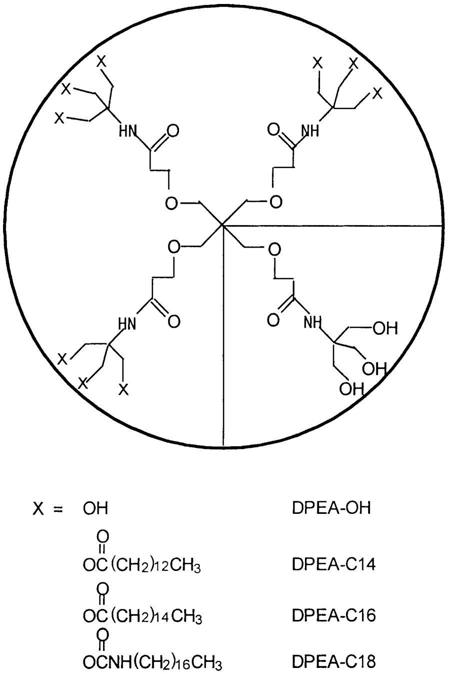

Fig. 1. Schematical outlines of DPEA-OH, DPEA-C14, DPEA-C16 and DPEA-C18.

Table 1
^{1}H NMR characterization data of unsubstituted and substituted dendritic polyetheramides

Sample	F (%)[a]	$\bar{M}_n$ (NMR)[b]
DPEA-OH	92	770
DPEA-C14$_{0.9}$	90	2850
DPEA-C16$_{0.9}$	89	3100
DPEA-C18$_{0.3}$	29	1710
DPEA-C18$_{0.6}$	58	2650
DPEA-C18$_{0.9}$	87	3600

[a] Substitution degree calculated from ^{1}H NMR spectra.
[b] Molar mass calculated from ^{1}H NMR spectra.

DPEA-C18$_{0.3}$, DPEA-C18$_{0.6}$ and DPEA-C18$_{0.9}$, respectively.

The results obtained from Perkin–Elmer Pyris 1 DSC measurements of all samples are listed in Table 2. The samples were at first heated from 25 to 155 °C at a rate of 40 °C min^{-1} and hold for 1 min at 155 °C, then cooled down to −70 °C at a rate of 300 °C min^{-1} by a liquid nitrogen system. It can be found that the T_g rises greatly for all grafted dendritic polyetheramides compared with DPEA-OH. Moreover, the rising of T_g appears to be dependent to the length of the alkyl chain attached, substitution degree and molecular structure of substitute. The T_g of DPEA-OH was considerably promoted from −20 to 12 °C upon the attachment of MC, however, to 22 °C upon the attachment of PC just because of two more methylene in alkyl chains. The effect also depends on the substitution degree, which has been obviously observed from the T_gs of 38, 43 and 48 °C for samples DPEA-C18$_{0.3}$, DPEA-C18$_{0.6}$ and DPEA-C18$_{0.9}$, respectively. It can also be found that T_gs of DPEA-C18 system are higher than those of DPEA-C14$_{0.9}$ and DPEA-C16$_{0.9}$.

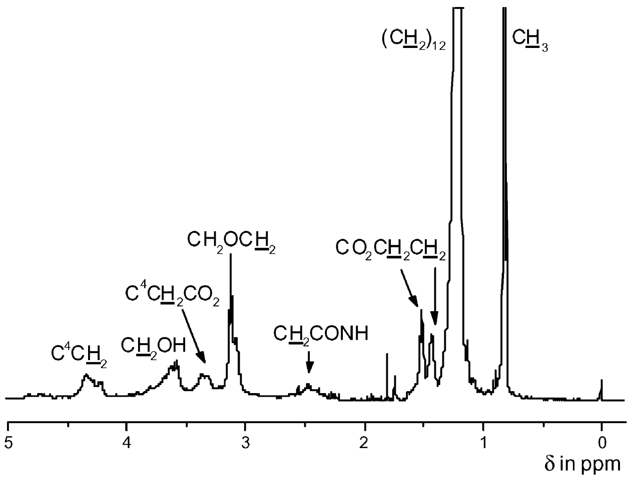

Fig. 2. ^{1}H NMR spectrum of DPEA-C16.

Reducing the density of the hydroxyl groups in higher substitution system leads to a decrease in hydrogen bonding, therefore, lowering the T_g. On the other hand, the introduction of longer alkyl chain results in an increase in the tendency of crystallization and the crystalline moiety forces DPEA-OH as an amorphous core into a more rigid structure. As a result, the T_g rises. In the case, the latter effect appears to be dominating factor, namely, the sample with longer end-alkyl chains or higher substitution degree has higher T_g due to be easier to crystallize for the substitutes. Therefore, the higher T_g of DPEA-C18 system compared with DPEA-C14$_{0.9}$ and DPEA-C16$_{0.9}$ can be attributed to both the less decrease of hydrogen bonding because of introducing new amide bond when modified with OI and the longer alkyl chains grafted.

In the cases of DPEA-C14$_{0.9}$ and DPEA-C16$_{0.9}$, there are three and four peaks in their DSC curves, respectively, while the DSC curves show two peaks in all DPEA-C18 systems. One explanation is that the multifunctional ester with a large number of long alkyl chains tends to form ordered mesophases before crystallization [5]. The other explanation is due to the presence of different types of crystallites [4].

As seen in Table 2, the melting point (T_m) depends slightly on the length of the alkyl chain attached and substitution degree. The T_m goes from 135 °C for DPEA-C14$_{0.9}$ down to 131 °C for DPEA-C16$_{0.9}$, and only varies in the range 114–118 °C for three DPEA-C18 systems with different substitution degree of 29, 58 and 87%.

However, the length of alkyl chain attached and substitution degree have a strong influence on the melting enthalpy (ΔH_m) and the rate of crystallization. DPEA-C14$_{0.9}$ possesses ΔH_m of 35 J g^{-1}, while ΔH_m of 117 J g^{-1}

Table 2
Differential scanning calorimeter characterization data of unsubstituted and substituted dendritic polyetheramides

Sample	T_g (°C)	ΔT_g (K)	T_m (°C)	ΔH_m (J g^{-1})	$t_{1/2}$ (s)[a]	T_g/T_m[b]	Comments
DPEA-OH	− 20		Nc[c]				
DPEA-C$14_{0.9}$	12	32	135	35	2.3	0.70	Three peaks
DPEA-C$16_{0.9}$	22	42	131	117	3	0.74	Four peaks
DPEA-C$18_{0.3}$	38	58	114	55	22.4	0.80	Two peaks
DPEA-C$18_{0.6}$	43	63	117	124	7.1	0.81	Two peaks
DPEA-C$18_{0.9}$	48	68	118	152	4.2	0.82	Two peaks

[a] Measuring at 110 °C.
[b] Using T_g and T_m in K.
[c] Noncrystalline.

for DPEA-C$16_{0.9}$ is obtained. DPEA-C$18_{0.3}$ with the substitution degree of 29% possesses a ΔH_m of 55 J g^{-1}, while the ΔH_m of 124 and 152 J g^{-1} are obtained for DPEA-C$18_{0.6}$ and DPEA-C$18_{0.9}$, respectively. For determining the rate of crystallization, the samples were at first heated from 5 to 155 °C at a rate of 40 °C min^{-1} and hold for 2 min at 155 °C, then cooled down to 110 °C at a rate of 150 °C min^{-1} and hold for 3 min at 110 °C, finally cooled down to 25 °C at a rate of 150 °C min^{-1}. The $t_{1/2}$ of DPEA-C$14_{0.9}$ is 2.3 s, while that of 3 s for DPEA-C$16_{0.9}$ is obtained. The $t_{1/2}$ of DPEA-C$18_{0.3}$ is 22.4 s, while 7.1 and 4.2 s are obtained for DPEA-C$18_{0.6}$ and DPEA-C$18_{0.9}$, respectively. Compared with those of DPEA-C$14_{0.9}$ and DPEA-C$16_{0.9}$, the higher $t_{1/2}$ of DEPA-C18 system attributes to blocking effect of the interaction of polar amide groups on chain movement. However, the increase of the rate of crystallization of DEPA-C18 system with the increase of the substitution degree of OI can be explained by the increase of the concentration of C18 alkyl chain as crystalline moiety.

From Table 2, it can also be found that T_g/T_m of DPEA-C$14_{0.9}$ and DPEA-C$16_{0.9}$ are both lower than 0.8. However, for the DPEA-C18 system all T_g/T_m values are over 0.8, which is similar to the phenomena in linear crystallizable block polymers [10]. In other words, crystallizable dendritic polymers DPEA-C18s can be considered as block copolymer analogues with dendritic core unit block and substitute unit block.

To further investigate the growth of crystallites, the powder samples were heated to the melt, then cooled slowly, and annealed well below their melting points. The micrographs obtained from the polarized light microscope have shown that all samples are heterogeneous on the scale length of the light microscope, as shown in Fig. 3. It can be found that the length of the alkyl chain attached and the substitution degree of the dendritic polymers have obvious influence on crystallite formation. The micrographs clearly demonstrate that the crystallite morphology of DPEA-C$14_{0.9}$ and DPEA-C$16_{0.9}$ is different from that of DPEA-C18 system. DPEA-C$14_{0.9}$ and DPEA-C$16_{0.9}$ form crystallites of about 20 and 50 μm, respectively, while the crystallites with the size of about 10, 20 and 60 μm are formed for DPEA-C$18_{0.3}$, DPEA-C$18_{0.6}$ and DPEA-C$18_{0.9}$, respectively. The increase of the size of crystallites may be explained by the decrease of the number of DPEA-OH as amorphous cores corresponding to the substitutes as crystalline moiety when increasing of the length of the substitutes and the substitution degree.

We conclude, therefore, that the semi-crystalline dendritic polyetheramides have been synthesized based on DPEA-OH by modifying the hydroxyl end-groups with MC, PC and OI in different substitution degrees. From the DSC measurements, T_g of DPEA-OH was improved sharply by attaching long alkyl chain and strongly affected by the length of the alkyl chain attached and the substitution degree. The T_m of these semi-crystallites depends slightly on the length of the alkyl chains attached and the substitution degree. However, both the length of the alkyl chains attached and the substitution degree have a strong influence on the ΔH_m and the rate of crystallization. Dendritic polymers of DPEA-C18 system can be considered as block copolymer analogues with dendritic core unit block and substitute unit block. From optical micrographs, it can be found that the size of crystallite was increased with the

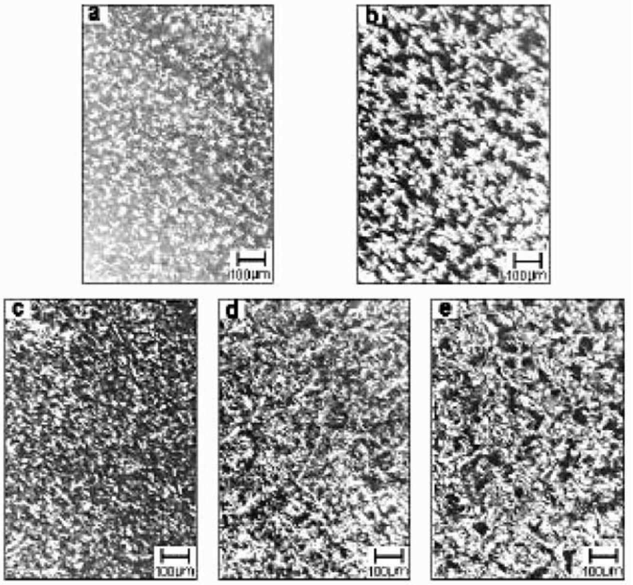

Fig. 3. Optical micrographs of (a) DPEA-C$14_{0.9}$, (b) DPEA-C$16_{0.9}$, (c) DPEA-C$18_{0.3}$, (d) DPEA-C$18_{0.6}$, and (e) DPEA-C$18_{0.9}$ at 10 °C.

increase of the length of the alkyl chain attached and the substitution degree.

Acknowledgements

The research work is supported by a grant (No. 20074034) from the Natural Science Foundation of China, which is gratefully acknowledged.

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