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Description	

Synthesis of well-defined hyperbranched polymers bio-based on multifunctional phenolic acids and their structure-thermal property relationships

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

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Abstract

A number of multifunctional AB_x-type monomers exist in plant metabolites, and studies on the formation of hyperbranching polymers from AB_x-type monomers are very significant in the development of bio-related polymeric materials. We established a method for the preparation of well-defined structures in bio-based, hyperbranched (HB) polyarylates by the copolycondensation of caffeic acid (DHCA) as an AB₂-monomer and *p*-coumaric acid (4HCA) as an AB-monomer, using the highly efficient catalyst Na₂HPO₄ to regulate the polymerization speed. ¹H NMR analysis revealed the time course of the formation of the hyperbranching structures, which strongly affected the glass transition and degradation temperatures, as well as the molecular weight and composition.

Keywords

Hyperbranched polymers, Bio-based polymers, Biomimetics, Polyarylates, NMR analyses.

1. Introduction

The importance of dendrimers and hyperbranched (HB) polymers has continuously drawn the attention of researchers during the last two decades due to their globular shape resulting from the branched backbone topology and their unique properties [1-6]. Although HB polymers have incomplete branched structures, they can be synthesized cost-efficiently and possess desirable properties similar to dendrimers. These attractive features have led to the development of novel synthetic routes for these polymers in this field [7, 8]. Most HB polymers are prepared by the polycondensation of AB_x-type monomers, such as AB₂ [9, 10], AB₃ [11–13], AB₄ [14, 15] and AB₆ [15] monomers, where the AB_x units play a role in the branching points. However, most of these AB_x-monomers are prepared via several steps, which preclude the rapid production of HB polymers on a large scale for industrial applications. Although many research groups have devoted themselves to developing facile, versatile, and cost-effective routes to synthesize HB polymers [16-26], only limited families of HB polymers have been prepared through the aforementioned methods.

On the other hand, there exist many AB_x-type multifunctional biochemicals such as glutamic acid, lysine, uronic acids, etc. We have focused on caffeic acid (3,4-dihydroxycinnamic acid; DHCA), which is an AB₂-type biomonomer with a polymerizable dihydroxyl-acid group. DHCA exists in most plants, belongs to the family of aromatic phytochemicals containing a *p*-coumaryl group, and is reported to

be biodegraded by microbial action [27]. From DHCA and *p*-coumaric acid (4-hydroxycinnamic acid; 4HCA), we have prepared high-performance functional bio-based polymers exhibiting good degradability and excellent thermomechanical performance [28-31]. However the effects of the branching structure on the thermal properties of these polymers have not been clarified yet, since the polymers showed too poor solubility to analyze their structure by spectroscopy.

Here, we developed a facile polymerization method using an appropriate catalyst that easily controls the reaction speed to prepare bio-based polyarylates, poly(DHCA-*co*-4HCA)s, with a well-defined structure. We then investigated their hyperbranching process and structure-thermal properties relationships in detail.

2. Experimental Section

The copolycondensation of 4HCA and DHCA was performed by in-bulk polymerization at an elevated temperature under a light-shield. The branching structures were analyzed by gel permeation chromatography (GPC) and ¹H nuclear magnetic resonance (¹H NMR), and the thermal properties were analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TGA). The details are shown in Supporting Information I.

3. Results and discussion

3.1 Synthesis

Aromatic HB polyesters, poly(4HCA-*co*-DHCA)s, were prepared based on the acidolysis polymerization of DHCA as the AB₂ monomer and 4HCA as the AB monomer using various alkaline catalysts (Scheme 1). First, we used a conventional catalyst such as CH₃COONa for the preparation of the poly(4HCA-*co*-DHCA)s, which showed multimodal GPC peaks indicative of a heterogeneous structure, presumably due to difficulty in controlling the side reactions. Next, we tried to find suitable catalysts for the production of copolyesters with well-defined structures, such as Na₂HPO₄, NaH₂PO₄, KH₂PO₄ and (CH₃COO)₂Zn. NaH₂PO₄, KH₂PO₄, and (CH₃COO)₂Zn only yielded oligomers with molecular weights of $M_w=9.9 \times 10^3$, $M_w=8.2 \times 10^3$, and $M_w=3.5 \times 10^3$, respectively, after 4 hours of polymerization at 200 °C. However, Na₂HPO₄ efficiently catalyzed those reactions generating polymers with a M_w of 6.1×10^4 and monomodal GPC peaks with a very narrow molecular weight distribution, which increased gradually with reaction time. As a result, it was concluded that Na₂HPO₄ was the most efficient catalyst for the polymerization of DHCA and 4HCA of the catalysts examined here. The good catalytic performance of Na₂HPO₄ can be attributed to its suitable alkalinity [32]. Using Na₂HPO₄ as a catalyst, a series of copolymers with in-feed compositions of DHCA (C_{DHCA}) of 75, 67, 60, 50, 40, and 25 were prepared (Table 1). The M_n values were in a narrow range of 21000-38200, whereas the M_w values were over a wide range of 52000-210700. As

a result, the molecular weight distribution (M_w/M_n) for C_{DHCA} of 25 and 75 mol% were more than 5, and were higher than the other copolymers with medium C_{DHCA} compositions of 67, 60, 50, and 40. Although a large number of DHCA units can raise the amount of AB_2 branching points to increase the M_w/M_n value, a large number of 4HCA units can form very rigid continuous segments of 4HCA to make the GPC peak broad.

3.2 Hyperbranching-process

In order to investigate the process of HB structure formation in the copolymer poly(4HCA-co-DHCA), GPC was used to monitor the polymerization process, permitting the evolution of molecular weight and branch architecture to be conveniently characterized that provide information with respect to the mechanistic hypothesis [33]. Fig. 1 shows changes in the GPC chromatogram as a function of the polymerization time. Two minor peaks appeared together with a main peak ($M_w = 10300$ and $M_w/M_n = 1.2$) in the chromatogram of oligomeric samples prepared for 2 hrs. After 4 hours, these two minor peaks disappeared, and only a monomodal peak with a symmetrical distribution ($M_w = 61000$ and $M_w/M_n = 2.8$) was detected. The monomodal peak became broader and shifted to a shorter retention time, meaning an increase in the molecular weight. After 8 hrs of polymerization, a very high molecular weight peak (more than 10×10^6 ; marked by the star) appeared, and increased its size with an increase in polymerization time from 8 to 16 hrs. In addition, the M_w/M_n increased slightly, which could be attributed to an increase in the branching degree (BD). Based on this consideration, the appearance of multimodal GPC peaks suggests

the presence of different components with different branching forms in the HB polymers [34].

The structures of these HB copolyesters were characterized by ^1H NMR (Fig. 2a). In particular, the COSY spectra showed sufficient resolution to assign these protons (Fig. S1; see for further discussion in Supplementary Information II). Detailed analyses using NMR spectroscopy were made to elucidate the precise structure and to quantify the BD of these copolymers. Since the number of acetyl groups equals the DHCA unit number plus one, it should be regarded as almost the same value as the number of DHCA units at a high polymerization degree. Therefore, it was hypothesized that the DHCA molar fraction, f_{DHCA} , to all units in poly(DHCA-*co*-4HCA) was almost the same as the content of acetyl groups estimated from the integral ratio of the proton signals from the acetyl groups to those of the aromatic rings. Fig. 3 is a representative plot of the f_{DHCA} change as a function of the polymerization time in poly(DHCA-*co*-4HCA)s with an in-feed C_{DHCA} of 60 mol%. It can be seen that f_{DHCA} was not constant during the polymerization; the f_{DHCA} decreased from 0.96 to 0.55 mol/mol, and the f_{DHCA} at 6 hrs of polymerization was almost the same as the C_{DHCA} . During the early stages of polymerization, the f_{DHCA} was much higher than the C_{DHCA} , supporting the higher reactivity of DHCA with two hydroxyls than 4HCA with only one hydroxyl groups. However, after 6 hours, the f_{DHCA} was lower than 0.6 mol/mol. The resulting f_{DHCA} was lower than the f_{DHCA} in the feed C_{DHCA} , which may be attributed to DHCA inactivation by oxidation over the long heat treatment time. Furthermore, similar f_{DHCA} changes were observed in the other

copolymers with different C_{DHCA} values (Figs. S3c and S4c).

The BD is one of the most important molecular parameters of HB polymers, because the BD characterizes the difference in the molecular structure from the linear analogs. NMR is a powerful tool for determining the BD value [35] for the purpose of studying the dynamic changes over the course of the HB polymerization. In order to investigate the process of HB polymer chain formation, we focused on a variety of acetyl groups in DHCA. If only one acetyl group of the diacetylated DHCA reacted, then a branching point would be not formed, and the residual acetyl groups became side chain acetyls. In this case, there are two side chain acetyls (*m*- and *p*-), as shown in Illustrations S_{DHCA} of Fig. 2b. Furthermore, one can confirm two acetyl end groups in DHCA (Illustration E_{DHCA} in Fig. 2b) and one end group in 4HCA (Illustration $E_{4\text{HCA}}$ in Fig. 2b). In total, five acetyl signals should be detected in the ^1H NMR of the copolymers. Fig. 2b shows a close-up view of the ^1H NMR spectrum over the chemical shift range of 2.35-2.55 ppm, focusing on the acetyl groups of poly(DHCA-*co*-4HCA) with a C_{DHCA} of 60 %, where one peak with various shoulders appeared. One can clearly separate the peak into five components, which were assigned to the above-mentioned five acetyl groups of poly(DHCA-*co*-4HCA). The end acetyl of 4HCA could be easily recognized by referring to the assignment of the DHCA homopolymers (only 4 acetyls; Fig. S2a). The DHCA related-acetyls could be assigned using the proton signals of the acetylated monomer as shown in Fig. 2b. In addition, the ^1H ^1H -NOESY spectrum of the polyDHCA homopolymer focusing on the correlation between the acetyl groups and the aromatic and double bonds

increased the reliability of this assignment; two signals marked by S_{DHCA} were multiply-correlated with those of the aromatic and double bonds, and were assigned to the side acetyl groups, whereas two signals marked by E_{DHCA} showed little correlation and thus were assigned to end acetyl groups (Fig. S2b). The signal marked by $E_{4\text{HCA}}$ was detected in the ^1H NMR spectra of the copolymers, poly(DHCA-*co*-4HCA)s, and then this signal should be assigned to the end acetyl groups of 4HCA. Based on the assignment, the integral ratios of the end acetyls to the total acetyls, $E/(S+E)$, were calculated, where S refers to the integral signal intensity of the side acetyls and E refers to the integral signal intensity of the end acetyls. Fig. 4a is a representative plot of $E/(S+E)$ in a copolymer with a C_{DHCA} of 60 mol%. During the initial 10 hrs of polymerization, the $E/(S+E)$ decreased with reaction time from 0.40 at 2 hours to 0.13 at 10 hours, and the ratio decreased most dramatically during the initial 4 hours. The end chain ratio decrease implies a decrease in the BD. On the other hand, with a further increase in the reaction time from 10 to 14 hrs, the $E/(S+E)$ increased slightly and then almost kept constant. Actually, the $E/(S+E)$ value was governed only by the DHCA units, because the BD was defined here as the branching unit molar ratios to all monomer units, and was simply calculated using equation [36],

$$\text{BD} = E / (S+E) \cdot f_{\text{DHCA}}$$

Fig. 4b shows the effect of the reaction time on the BD of poly(DHCA-*co*-4HCA) with a C_{DHCA} of 60 mol%. The BD decreased with the reaction time from 2 to 10 hrs, but increased from 10 to 16 hrs. During the first 2 hrs of polymerization, the BD was

high at 0.39 because the DHCA, which has a higher reactivity than 4HCA, was consumed preferentially at the beginning of polymerization to create small hyperbranching oligomers (from A to B in Fig. 5). However, the BD declined drastically from 0.39 at 2 hrs to 0.15 at 4 hrs. Further branching of the small oligomers may have been difficult due to steric hindrance, and thus main chain propagation was favored, causing the rapid BD decline. The degree of decline decreased as the reaction time increased from 4 to 10 hrs, and then became almost constant at 0.07-0.09 up to 14 hrs, because further polymerization elongated the main chain while the branching reactions occurred occasionally due to reduced steric hindrance (from B to D in Fig. 5). After 14 hrs, the BD increased again to make the chain ends highly dense, presumably due to the HB reaction caused by a monomer or polymer chain reaction with the residual acetyl groups to create large polymers with M_w values more than 10^7 (from D to E in Fig. 5).

It should be noted that the branching degree of the copolymer was not high, even at the last stage of polymerization, which may be attributed to the following reasons. One of two hydroxyls of DHCA reacted with carboxylic acid as efficiently as the hydroxyl of 4HCA, to create the polycoumarate backbone. However the reactivity of another hydroxyl of DHCA might be remarkably reduced by steric hindrance of the already-formed backbone.

3.3. Thermal properties

Although hyperbranched-polymers are usually difficult to be processed, these

copolymers showed fairly heat-processable (Fig. 5(b)). Thermal behavior such as the glass transition and thermal degradation are key factors for the utilization of these polymers in industrial applications.

Theoretically, the glass transition temperature should decrease upon increasing the free volume fraction in polymeric materials [37]. The free volume is larger in a polymer with a higher chain-end composition to the entire chain. Therefore, the T_g value is strongly dependent on the molecular weight and the flexibility of the polymer chains. The relationship between the T_g vs reaction time and the T_g vs f_{DHCA} in poly(DHCA-co-4HCA)s with C_{DHCA} values of 40 and 60 mol% are summarized in Fig. 6 and Fig. 7, respectively. Fig. 6 shows that the T_g increased with a decrease in the reaction time to 8 h, became almost constant from 8 h to 12 h, but then unexpectedly increased again at over 12 h. As seen from Fig. 1, the M_w increased with increasing reaction time, although the GPC peaks were multimodal and contributed strongly to the increased T_g . When the M_w values were very high at polymerization times over 8 h, the effects of further M_w increases on the decrease in the chain end composition were trivial, and thus the T_g became almost constant. However, the further T_g increase with the reaction times over 12 h could not be explained simply by an increase of M_w . The value of the f_{DHCA} decreased throughout the entire polymerization reaction as shown in Fig. 3, which contributed to the increase in the T_g in both copolymer systems with in feed C_{DHCA} of 40 mol% and 60 mol% (Fig. 7), because of the reduced flexibility in the copolymer with an increased 4HCA composition. Therefore, it was difficult to postulate that the f_{DHCA} had any effect on

the T_g increase at only over 12 h. On the other hand, Fig. 4b shows that the BD was almost constant over the polymerization time range from 6 h to 10 h, but increased again at over 12 h (also seen in Fig. S3b and Fig. S4b), which was in agreement with the polymerization time for further T_g increases. Although the BD decrease at the beginning of polymerization may also be effective in causing the T_g to change, it could be considered to have a much smaller effect than the M_w increase on the T_g because the free volume of such a short polymer chains over this polymerization time was strongly affected by the M_w change. Consequently, the further T_g increase in the polymerization range over 12 h was mainly due to the BD increase, presumably caused by the increased density of polymer chain ends restricting molecular mobility to decrease the contribution of the polymer chain ends to the free volume. It had been attempted to investigate the T_g property of poly4HCA for further disclosing of the relationship between homopolymer and copolymer, but no T_g was observed in poly4HCA probably due to highly crystallinity in the homopolymer.

The thermal stability of poly(DHCA-co-4HCA)s was also estimated from the weight loss change upon increasing the temperature by thermogravimetry. A thermogravimetric curve of poly(DHCA-co-4HCA) with a C_{DHCA} of 60 mol% is shown in Fig. 8. The results for the 10 % weight loss temperature, T_{10} , versus the polymerization time are summarized in Fig. 9. From 2 h to 4 h, the polymer showed poor stability, probably due to the low molecular weight. However, the thermal stability increased significantly from a T_{10} of 218 °C at 2 h to a T_{10} of 353 °C at 6 h, owing to M_w increase effects. Interestingly, the thermal stability went down from a T

T_{10} of 353 °C at 6 h to 331 °C at 12 h, and then the highest thermal stability was shown in the polymer incubated for 6 h. The T_{10} decrease might be due to a decrease in the f_{DHCA} because the homopolymer polyDHCA showed a higher degradation temperature than the poly4HCA [30]. However, a higher thermal stability at 16 h (a T_{10} of 343 °C) than at 12 h (a T_{10} of 331 °C) was obviously observed from Fig. 9, which could be mainly attributed to a very high BD leading to an increased inter-branch force and thermal-decomposition temperature. A similar phenomenon in thermal stability can also be found in the polymerization of poly(DHCA-*co*-4HCA) with a C_{DHCA} of 40 mol% and a C_{DHCA} of 50 mol% (Fig. S5 and Fig. S6).

Furthermore, thermal stability of poly(DHCA-*co*-4HCA) was compared with non-branched homopolymer poly4HCA, which showed a lower degradation temperature, T_{10} of 280 °C than those of poly(DHCA-*co*-4HCA)s with BD of around 0.1 prepared by polymerization for more than 6 h. Although BDs in copolymers were not high, T_{10} values were much higher than that of non-branching homopolymer, which suggests that appropriate branching in poly(DHCA-*co*-4HCA)s played important role in increasing thermal decomposition.

3.4. Solubility

The solubility of the poly(DHCA-*co*-4HCA) with different C_{DHCA} values in DMF was evaluated (Table 2). The 4HCA homo-polymer poly4HCA is insoluble in DMF, whereas polyDHCA dissolved in DMF. The solubility of the copolymers increased with increasing C_{DHCA} . In the poly(DHCA-*co*-4HCA)s with C_{DHCA} values from 25 to 40, the polymers prepared for shorter polymerization times were soluble in DMF,

whereas the ones prepared for the longer polymerization times were insoluble. Overly-dense branching chains might restrict the chain mobility and solubilization of the polymer chains. The poly(DHCA-*co*-4HCA)s with C_{DHCA} values of 60, 67, and 75, as well as polyDHCA can be completely dissolved in DMF, even if the polymerization time was very long, thus resulting in a very high molecular weight.

4. Conclusion

We described a facile method for the one-pot synthesis of well-defined biodegradable hyperbranched polyesters, poly(DHCA-*co*-4HCA)s, in the presence of Na_2HPO_4 as an effective catalyst, from bio-available monomers of caffeic acid as a multifunctional AB_2 unit and *p*-coumaric acid as an ordinal AB unit. The polymer structures such as the copolymer composition and branching degree were investigated by ^1H NMR spectroscopy. Three stages of the hyperbranching process are proposed; in the first stage, DHCA-rich oligomers with short branches and a high branching degree were formed. During the second stage, the main chain was preferentially propagated, accompanied by a slow decrease in the BD. In the third stage, a preferential branching reaction was caused by monomer reactions with the side acetyl groups of the polymers. This hyperbranching strongly affected the glass transition temperature and degradation temperature of the polymers. The glass transition temperature increased with an increasing in the molecular weight, and saturated at a threshold polymerization time, but then increased again following further polymerization for over 12 h. The degradation temperature also showed an

unexpected increase at over 12 h. Further polymerization for over 12 h induced an increase in the BD, thus increasing the density of the polymer chain ends, which restricted the molecular mobility of the chain ends. As a result, the extremely high density of polymer chain ends enhanced their thermal stability. The results obtained here can lead to new applications in various fields such as biomedical and environmental materials with biodegradable properties.

Supporting Information Available

Experimental section, Structural characterizations of copolyesters, Additional datasets of DB, S/(S+E), Additional TGA curves and thermal degradation figures.

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Table 1 Molecular weights of poly(DHCA-*co*-4HCA)s with different in-feed compositions of DHCA^a

C _{DHCA} ^b (mol%)	<i>M_w</i> (g/mol)	<i>M_n</i> (g/mol)	<i>M_w/M_n</i>	Yield ^c
25	210700	32400	6.51	75
40	125900	38200	3.30	78
50	91300	21100	4.42	76
60	52000	21000	2.50	85
67	83000	27100	3.05	81
75	170900	31300	5.46	80

^a Reactions were carried out in the presence of Na₂HPO₄ (1 wt% to total weight of monomers) and acetic anhydride (120 mL) at 150 °C for 2 hrs at atmosphere pressure and then at 200 °C under vacuum till the reaction mixture became solid for 6-12 hrs.

^b DHCA molar composition to the total monomers in feed.

^c Purification by precipitation.

Table 2

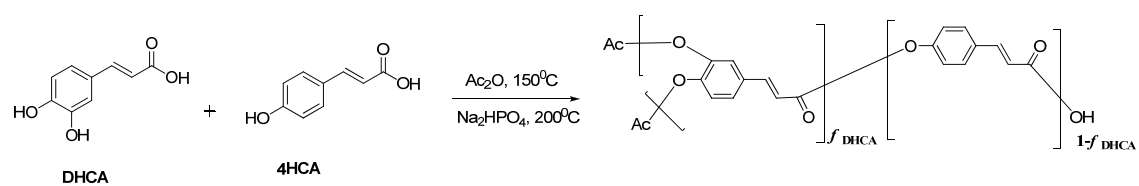
Solubility of homo-polymers and copolymers poly(DHCA-*co*-4HCA) with different in-feed compositions of DHCA in DMF^a

C _{DHCA} in feed ^b	Polymerization time							
	2h	4h	6h	8h	10h	12h	14h	16h
0	-	-	-	N	N	N	N	N
25	+	+	+	±	±	±	-	-
33	+	+	+	±	±	±	±	-
40	+	+	+	+	±	±	±	-
50	+	+	+	+	+	±	±	±
60	+	+	+	+	+	+	+	+
67	+	+	+	+	+	+	+	+
75	+	+	+	+	+	+	+	+
100	+	+	+	+	+	+	+	+

^a Marks “+”, “-”, “±” means soluble, insoluble, and partly soluble, respectively.

^bSolubility was checked using DMF solvent with concentration 10 mg/10 ml and

C_{DHCA} refers to the composition of DHCA.



Scheme 1. Syntheses of the copolymers of poly (DHCA-*co*-4HCA)s

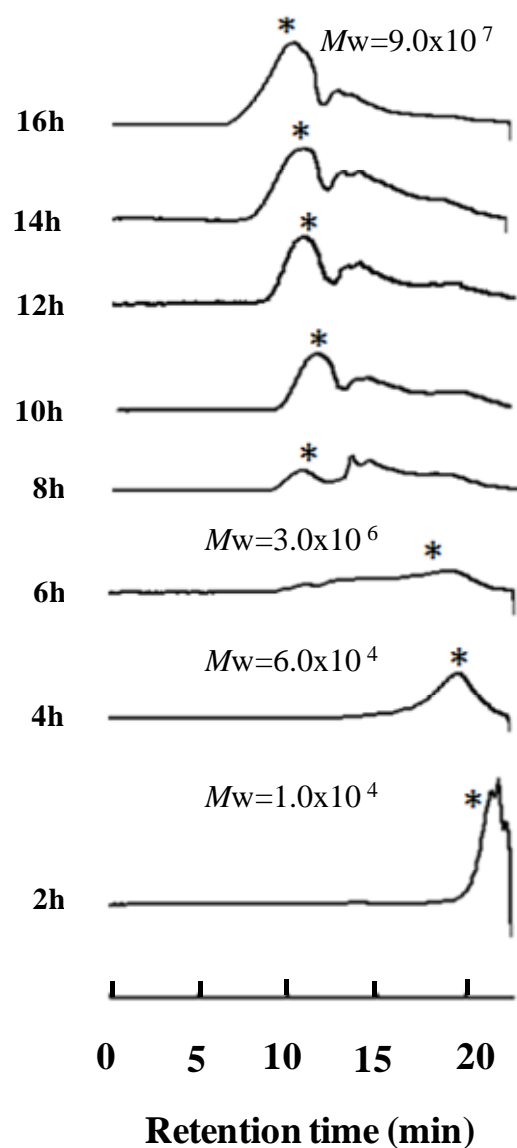


Fig. 1. Changes in the GPC chromatograms as a function of the polymerization time in poly(4HCA-*co*-DHCA) with a DHCA in-feed of 60 mol %.

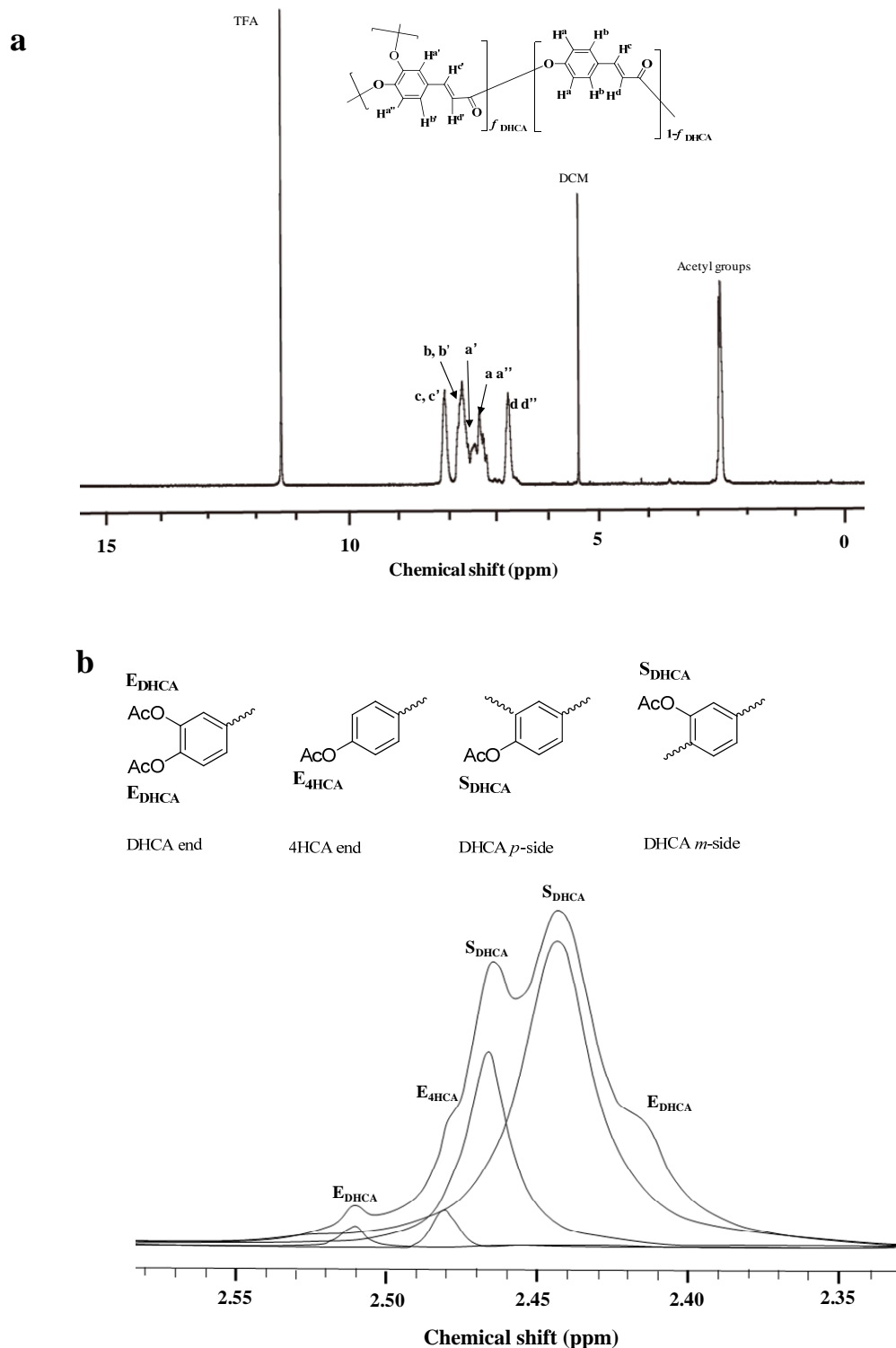


Fig. 2. (a) ^1H NMR spectrum of poly(DHCA-*co*-4HCA) with an in-feed monomer composition of $C_{\text{DHCA}} = 60$ mol%. (b) Close-up of the ^1H NMR spectrum focusing on the acetyl groups of poly(DHCA-*co*-4HCA) over a chemical shift range between 2.35-2.55 ppm. The acetyl peaks were composed of two small peaks marked by DHCA end chains, E_{DHCA} , two peaks marked by DHCA side chains, S_{DHCA} and one peak marked by 4HCA end chain, $E_{4\text{HCA}}$, in the spectrum, above which the corresponding structures are shown.

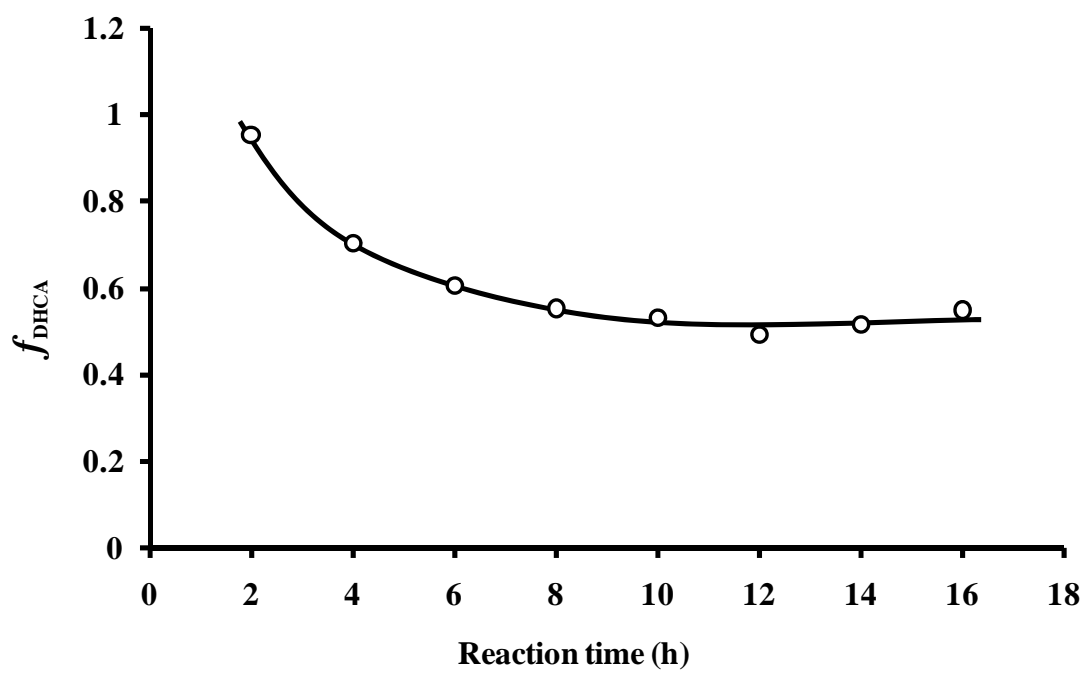


Fig. 3. Influence of the reaction time on the percentage of DHCA in poly(DHCA-co-4HCA) with a C_{DHCA} of 60 mol%.

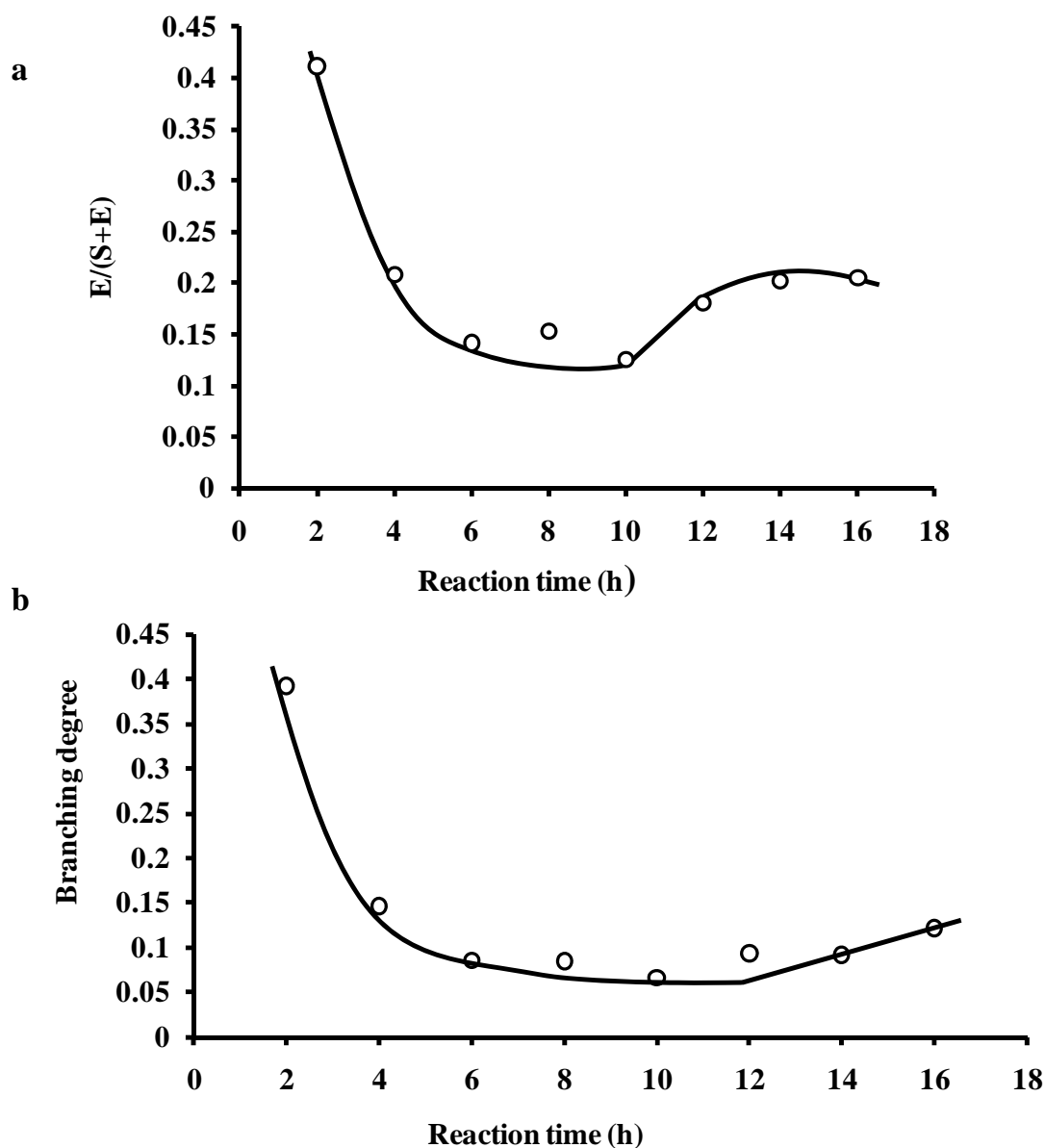


Fig. 4. (a) Influence of the reaction time on the ratio of $E/(S+E)$ in the polymerization reaction of poly(DHCA-*co*-4HCA) with a C_{DHCA} of 60 mol%. S: side groups, E: end groups. $E/(S+E)$: ratio of side group to all acetyl groups. (b) Influence of the reaction time on the hyperbranching degree in the polymerization reaction of poly(DHCA-*co*-4HCA) with a C_{DHCA} of 60 mol%.

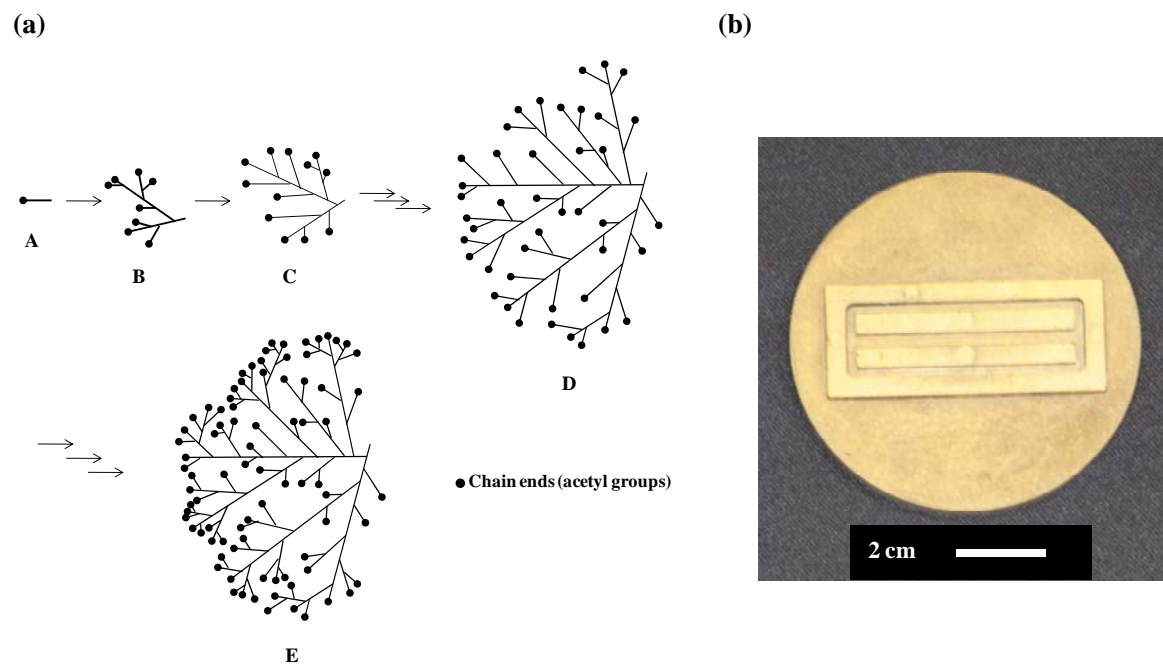


Fig. 5. (a) Proposed scheme for the hyperbranching process for the copolymerization of DHCA with 4HCA. (b) Inset: photo of processed resin p(DHCA-co-4HCA) copolymer.

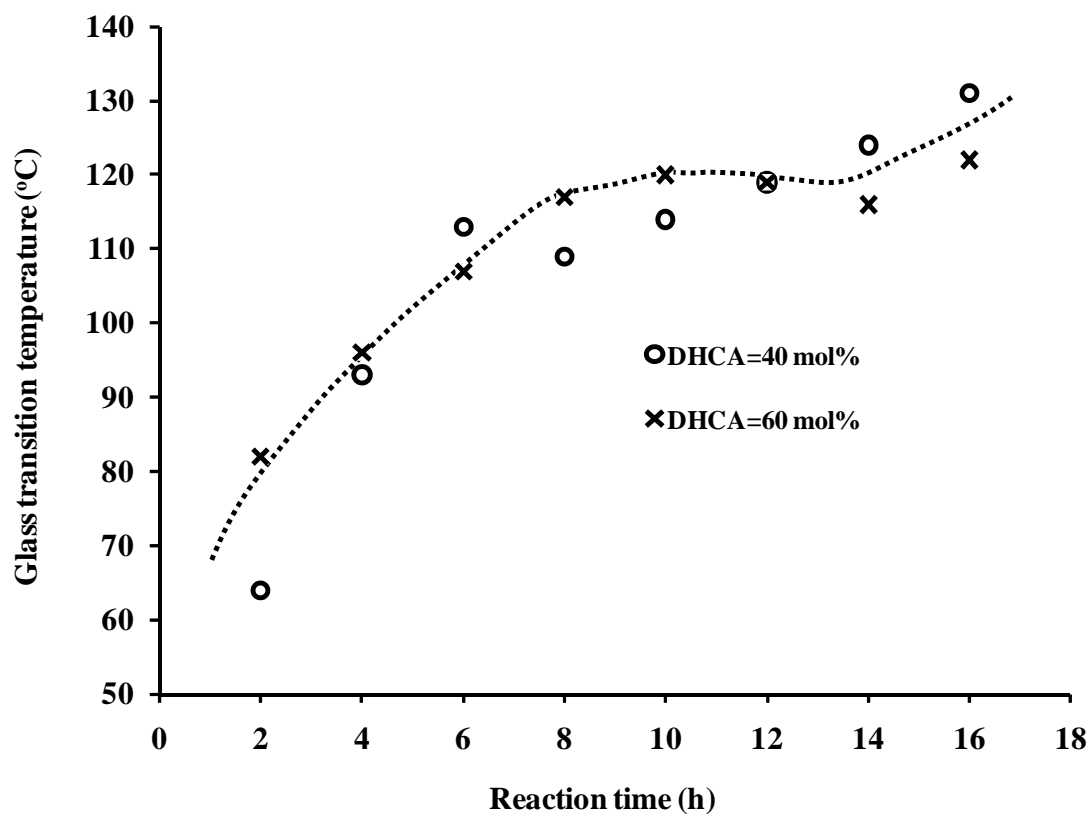


Fig. 6. T_g versus different polymerization time in poly(DHCA-co-4HCA) with an in-feed monomer composition of $C_{\text{DHCA}} = 60$ mol % and an in-feed monomer composition of $C_{\text{DHCA}} = 40$ mol %.

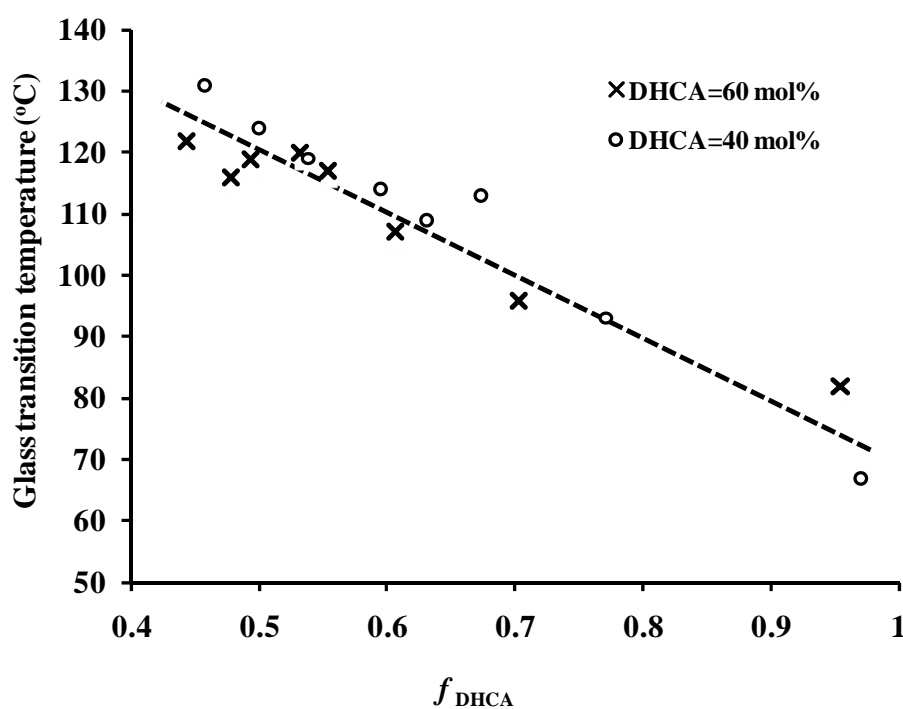


Fig. 7. T_g versus composition of the f_{DHCA} in copolymerization of poly(DHCA-*co*-4HCA) with an in-feed monomer composition of $C_{\text{DHCA}} = 60$ mol % and an in-feed monomer composition of $C_{\text{DHCA}} = 40$ mol %.

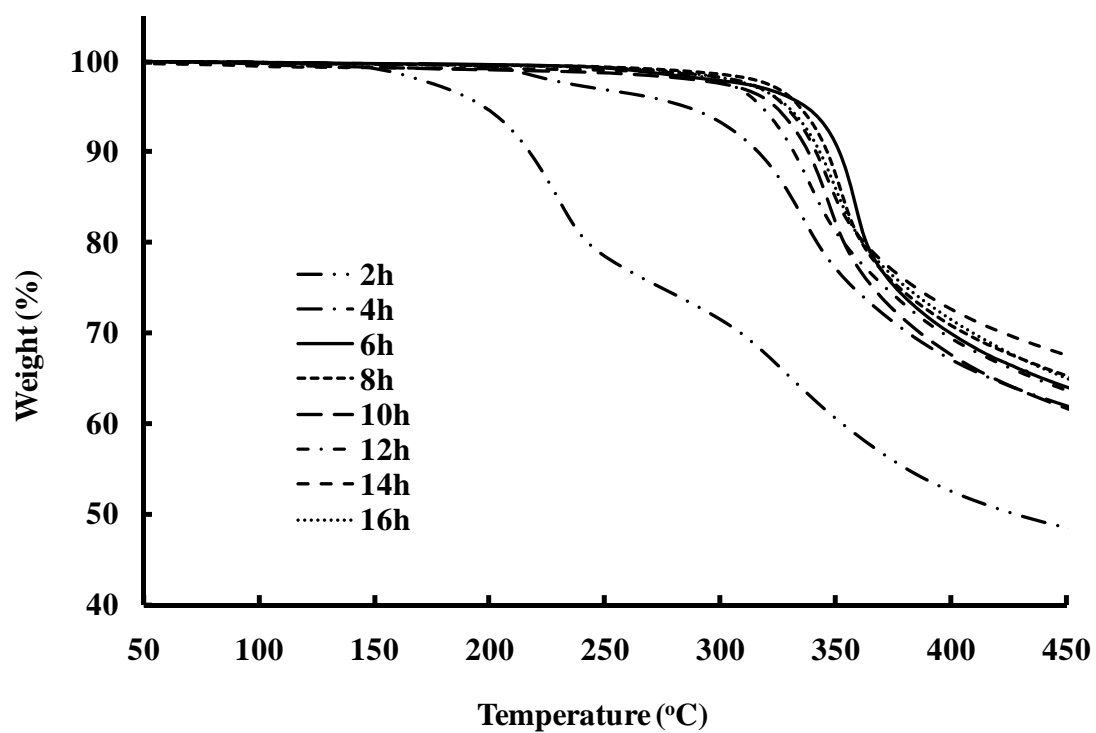


Fig. 8. TGA curve of poly(DHCA-co-4HCA) with an in-feed monomer composition of $C_{\text{DHCA}} = 60$ mol% in nitrogen.

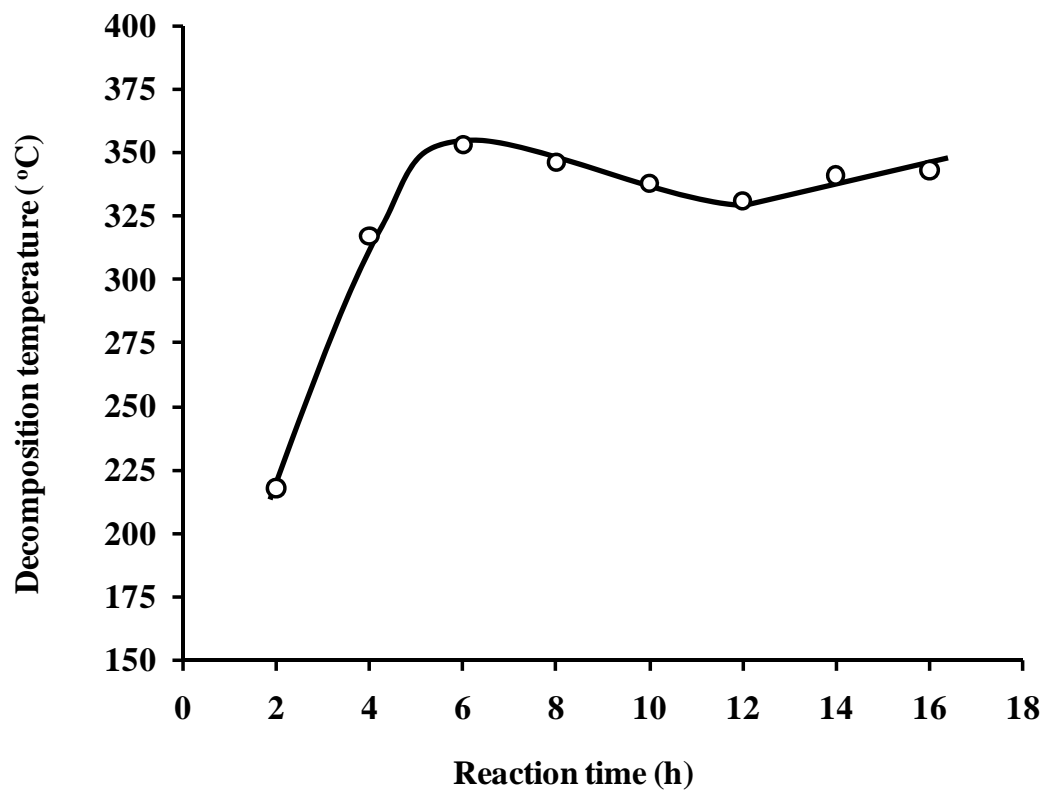


Fig. 9. T_{10} versus copolymerization reaction time of poly(DHCA-*co*-4HCA) with an in-feed monomer composition of $C_{\text{DHCA}} = 60$ mol %.