

STUDY OF GRAFT SITES IN EPOXY GRAFT COPOLYMERS BY QUANTUM CHEMISTRY CALCULATIONS*

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Abstract Exploration and characterization of grafting productions by experimental methods are often cumbersome or sometimes impossible. Therefore, quantum chemistry calculations were performed to characterize the graft sites of epoxy resin. According to the Gibbs free energy criterion of the second law of thermodynamic, the reported graft sites were confirmed, and more important, some unreported graft sites were found. In addition, method of increasing the number of graft sites was studied in this article.

Keywords: Epoxy resin; Free radical; Graft site.

INTRODUCTION

Water-borne coatings have been used to reduce pollution, and it has enjoyed tremendous success. In the modern coating industry, epoxy resins are used extensively, and there are two ways to disperse epoxy resin in water^[1, 2]. One is dependent on external emulsifier to disperse the resin in water. The other is by way of chemical modification to introduce polar groups, especially by grafting copolymerization. Graft copolymers have been known for many years for their unique properties which cannot be obtained from homopolymer alone, and the synthesis^[3, 4] and characterization^[5, 6] of epoxy-acrylic graft copolymers have been described.

In previous articles, bisphenol-A-epichlorohydrin epoxy resins were used to identify graft sites by ¹³C-NMR spectroscopy and suggested that the grafting was achieved by using a very high level of free radical initiator and take place at the aliphatic backbone portion ($-\text{CH}_2-\text{C}(\text{OH})\text{H}-\text{CH}_2-$) of the epoxy resins (the middle bold segment — segment 1 in Fig. 1)^[7–10].

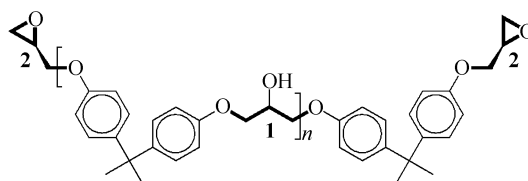


Fig. 1 Chemical structure of epoxy resin

But, up to now, whether the other secondary and tertiary hydrogen in epoxy resin (the other bold segments — segment 2 in Fig. 1) should be abstracted or not hasn't been reported yet. This is because that most free-radical-induced graft copolymerizations not only lead to the desired graft copolymers but also to homopolymers

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and other side-reactions, consequently, the exploration and detailed characterization of grafting products by experimental methods are often cumbersome or sometimes impossible even by recent analytical techniques.

Therefore, quantum chemistry calculations were performed, in this work, to characterize the graft sites of bisphenol-A-epichlorohydrin epoxy resin, and a middle molecular weight epoxy resin —ER was used as the model compound (see Fig. 2).

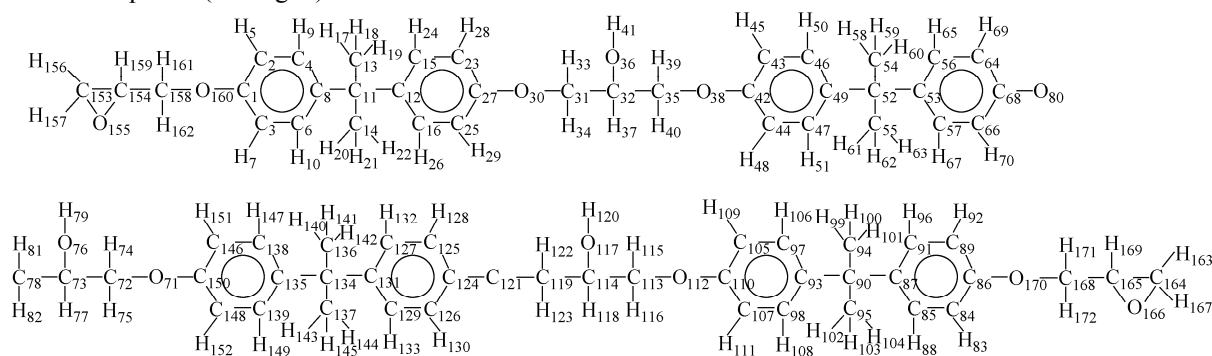


Fig. 2 Chemical structure of ER

Moreover the level of free radical initiator plays an important role in the preparation of graft copolymers. Therefore the effects of free radicals (see Fig. 3) on graft polymerization were discussed in this work. In addition, the method of increasing the number of graft sites was also discussed.

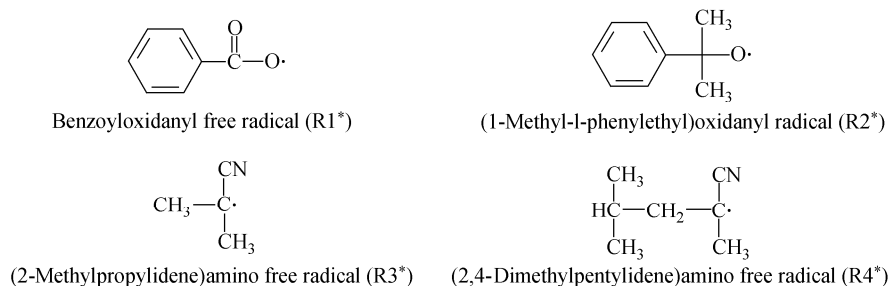


Fig. 3 Chemical structure of free radical

COMPUTATIONAL

Quantum chemical density functional calculations were carried out with 03 version of Gaussian suite of program^[11] using the B3LYP^[12, 13] functions of density functional theory (DTF). Frequencies were calculated to verify stationary points as stable states for the B3LYP/STO-3G optimized conformations of ER and for the B3LYP/6-31G(d) optimized conformations of all the other compounds. Unscaled frequencies were used to calculate zero point energies (ZPE) and thermal corrections to Gibbs energy (G_{corr}) at six temperatures. Single-point energies (SPE) were computed at B3LYP/6-311 + g(d, p) level of theory from the optimized stable state. The final energies (E) were calculated as the sum of SP and ZPE ($E = \text{SP} + \text{ZPE}$), the Gibbs energies were calculated as the sum of SP and G_{corr} ($G = \text{SP} + G_{\text{corr}}$).

The hydrogen-abstraction reactions discussed in this work are given in the following chemical equations. ER* represent macroradical formed by hydrogen-abstraction from the backbone of ER. R1-H, R2-H, R3-H and R4-H represent the hydrogen-abstraction products of R1*, R2*, R3* and R4*, respectively.

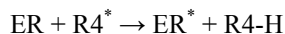
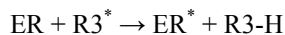
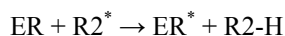
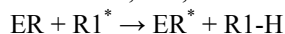


Table 1. ΔG of hydrogen-abstraction reactions of reported graft sites

ER*	T	R1*	R2*	R3*	R4*	ER*	T	R1*	R2*	R3*	R4*
C ₃₁ —H ₃₃ *	298	-0.61	-0.47	0.29	0.45	C ₇₈ —H ₈₁ *	298	-0.33	-0.20	0.57	0.72
	303	-0.61	-0.47	0.30	0.45		303	-0.33	-0.20	0.57	0.73
	333	-0.61	-0.48	0.30	0.45		333	-0.31	-0.18	0.60	0.75
	363	-0.61	-0.48	0.30	0.45		363	-0.29	-0.16	0.62	0.77
	393	-0.62	-0.49	0.30	0.45		393	-0.27	-0.14	0.64	0.80
C ₃₁ —H ₃₄ *	423	-0.62	-0.49	0.30	0.45	C ₇₈ —H ₈₂ *	423	-0.25	-0.12	0.67	0.82
	298	-0.50	-0.37	0.40	0.55		298	-0.23	-0.09	0.68	0.83
	303	-0.51	-0.37	0.40	0.55		303	-0.22	-0.09	0.68	0.84
	333	-0.51	-0.37	0.40	0.55		333	-0.20	-0.07	0.70	0.86
	363	-0.51	-0.38	0.40	0.55		363	-0.18	-0.05	0.73	0.88
C ₃₂ —H ₃₇ *	393	-0.51	-0.38	0.40	0.55	C ₁₁₃ —H ₁₁₅ *	393	-0.16	-0.03	0.75	0.90
	423	-0.52	-0.39	0.40	0.55		423	-0.14	-0.01	0.78	0.93
	298	-0.55	-0.42	0.35	0.50		298	-0.47	-0.33	0.43	0.59
	303	-0.55	-0.42	0.35	0.51		303	-0.47	-0.33	0.44	0.59
	333	-0.55	-0.42	0.35	0.51		333	-0.46	-0.33	0.44	0.60
C ₃₅ —H ₃₉ *	363	-0.56	-0.42	0.36	0.51	C ₁₁₃ —H ₁₁₆ *	363	-0.46	-0.33	0.45	0.60
	393	-0.56	-0.43	0.36	0.51		393	-0.46	-0.33	0.46	0.61
	423	-0.56	-0.43	0.36	0.51		423	-0.46	-0.33	0.46	0.61
	298	-0.49	-0.35	0.41	0.57		298	-0.43	-0.29	0.47	0.63
	303	-0.49	-0.35	0.41	0.57	C ₁₁₄ —H ₁₁₈ *	303	-0.43	-0.29	0.47	0.63
C ₃₅ —H ₄₀ *	333	-0.49	-0.36	0.42	0.57		333	-0.42	-0.29	0.48	0.64
	363	-0.49	-0.36	0.42	0.58		363	-0.42	-0.28	0.49	0.65
	393	-0.49	-0.36	0.43	0.58		393	-0.41	-0.28	0.50	0.66
	423	-0.49	-0.36	0.43	0.58		423	-0.41	-0.28	0.51	0.66
C ₇₂ —H ₇₄ *	298	-0.52	-0.38	0.39	0.54		298	-0.55	-0.41	0.35	0.51
	303	-0.52	-0.38	0.39	0.54	C ₁₁₉ —H ₁₂₂ *	303	-0.55	-0.41	0.35	0.51
	333	-0.52	-0.39	0.39	0.54		333	-0.55	-0.41	0.36	0.51
	363	-0.52	-0.39	0.39	0.54		363	-0.55	-0.41	0.37	0.52
	393	-0.53	-0.40	0.39	0.54		393	-0.54	-0.41	0.37	0.52
C ₇₂ —H ₇₅ *	423	-0.53	-0.40	0.39	0.54		423	-0.54	-0.41	0.38	0.53
	298	-0.49	-0.35	0.42	0.57	C ₁₁₉ —H ₁₂₃ *	298	-0.55	-0.42	0.35	0.51
	303	-0.49	-0.35	0.42	0.57		303	-0.55	-0.42	0.35	0.51
	333	-0.49	-0.35	0.42	0.58		333	-0.55	-0.42	0.36	0.51
	363	-0.49	-0.35	0.43	0.58		363	-0.55	-0.42	0.36	0.51
C ₇₃ —H ₇₇ *	393	-0.48	-0.35	0.43	0.58		393	-0.55	-0.42	0.37	0.52
	423	-0.48	-0.35	0.44	0.59		423	-0.55	-0.42	0.37	0.52
	298	-0.51	-0.37	0.40	0.55		298	-0.47	-0.34	0.43	0.58
	303	-0.51	-0.37	0.40	0.55		303	-0.47	-0.34	0.43	0.58
	333	-0.51	-0.38	0.40	0.55		333	-0.47	-0.34	0.43	0.59
	363	-0.51	-0.38	0.40	0.55		363	-0.47	-0.34	0.44	0.59
	393	-0.52	-0.38	0.40	0.55		393	-0.47	-0.34	0.44	0.59
	423	-0.52	-0.39	0.40	0.55		423	-0.48	-0.35	0.44	0.59
	298	-0.51	-0.38	0.39	0.55						
	303	-0.51	-0.38	0.39	0.55						
	333	-0.51	-0.38	0.40	0.55						
	363	-0.51	-0.37	0.40	0.56						
	393	-0.50	-0.37	0.41	0.56						
	423	-0.50	-0.37	0.42	0.57						

All the values of temperature are in K and energies are in eV.

For these reactions, the Gibbs free energy of reactions (ΔG) was computed as the difference of Gibbs free energies between reactants and products ($\Delta G = \sum G_{\text{Products}} - \sum G_{\text{Reactants}}$), and the carbon-hydrogen (C—H) bond

dissociation energies (BDE) of epoxy resin were computed as the energy difference between the dehydrogenation fragment and epoxy resin ($BDE = E_{\text{Macroradical}^*} + E_{\text{H}^*} - E_{\text{Epoxy resin}}$).

RESULTS AND DISCUSSION

Molecular Properties of the Reported Graft Sites

Effects of free radicals and temperature on the hydrogen-abstraction reaction of the reported graft sites

The level of free radical plays an important role in the hydrogen-abstraction reaction, and a higher level of free radical favors a higher level of grafting. Therefore, ΔG of reported hydrogen-abstraction reactions induced by different free radicals at different temperatures were calculated and listed in Table 1.

As can be seen from Table 1 that, ΔG of reactions increased with the increasing of temperature, and all the hydrogen-abstraction reactions induced by $R1^*$ and $R2^*$ have negative ΔG while the ones induced by $R3^*$ and $R4^*$ are positive. According to the second law of thermodynamics, reactions with negative ΔG are spontaneous. Therefore, all the reported positions in epoxy resin were conformed as graft sites when induced by proper free radicals ($R1^*$, $R2^*$).

C—H bond length and dissociation energy of the reported graft sites

One method of estimating the difficulty level of hydrogen-abstraction is to compute it as the C—H bond length, therefore the C—H bond length of reported graft sites were calculated, and the computations were conducted on simplified structure representatives of the reported graft sites (see Fig. 4).

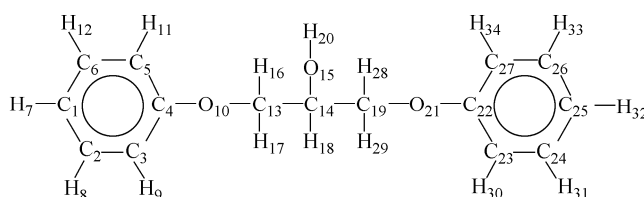


Fig. 4 Model compound of epoxy resin containing the reported graft sites

All the C—H bond lengths of reported graft sites in model compound were listed in Table 2. As can be seen, all the C—H bond lengths are in the range of 0.1096–0.1101 nm and this range will be used as a reference for the hydrogen-abstraction study of the potential graft sites.

Table 2. C—H bond length of model compound containing reported graft sites

Bonds	Bond length (nm)	Bonds	Bond length (nm)
C ₁₃ —H ₁₆	0.1099	C ₁₃ —H ₁₇	0.1098
C ₁₄ —H ₁₈	0.1101	C ₁₉ —H ₂₈	0.1096
C ₁₉ —H ₂₉	0.1099		

In addition, C—H bond dissociation energies of reported graft sites in ER were calculated and listed in Table 3. All the C—H bond dissociation energies of reported graft sites are in the range of 3.84–4.01 eV and this range will also be used as a reference for the study of the potential graft sites.

Table 3. C—H bond dissociation energies of reported graft sites

Bonds	BDE (eV)	Bonds	BDE (eV)	Bonds	BDE (eV)
C ₃₁ —H ₃₃	3.84	C ₃₁ —H ₃₄	3.95	C ₃₂ —H ₃₇	3.89
C ₃₅ —H ₃₉	3.93	C ₃₅ —H ₄₀	3.95	C ₇₃ —H ₇₇	3.90
C ₇₂ —H ₇₄	3.93	C ₇₂ —H ₇₅	3.95	C ₇₈ —H ₈₁	3.90
C ₇₈ —H ₈₂	4.01	C ₁₁₄ —H ₁₁₈	3.87	C ₁₁₃ —H ₁₁₅	3.93
C ₁₁₃ —H ₁₁₆	3.95	C ₁₁₉ —H ₁₂₂	3.85	C ₁₁₉ —H ₁₂₃	3.95

Selection of the Potential Graft Sites

According to the molecular orbital theory, the hydrogen-abstraction reaction is governed by the highest occupied molecular orbital (HOMO) of ER and single occupied molecular orbital of free radicals. Therefore HOMO of ER was calculated and its surface was plotted in Fig. 5.

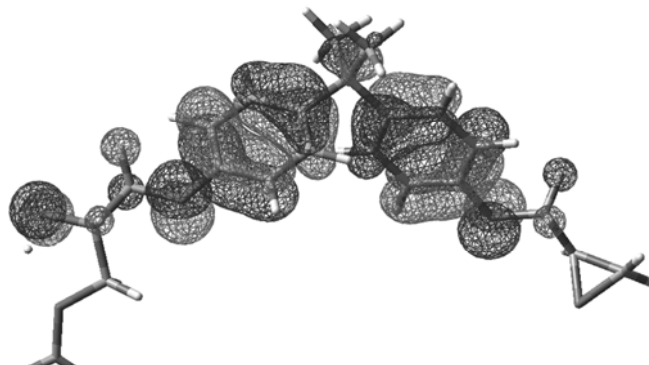


Fig. 5 The highest occupied molecular orbital of epoxy resin

As shown in Fig. 5, the HOMO of ER is mainly on the benzene ring, oxygen and hydrogen. The hydrogen includes not only the reported ones but also the ones bonded with phenyl ether and epoxy groups (see segment 2 in Fig. 1). Therefore segment 2 in Fig. 1 was selected as the potential graft sites, and their molecular properties were presented in the following.

Molecular Properties of the Potential Graft Sites

Effects of free radicals and temperature on the hydrogen-abstraction reaction of potential graft sites

For the same reason, ΔG of all potential hydrogen-abstraction reactions induced by different free radicals at six temperatures were calculated and listed in Table 4.

As can be seen from Table 4, ΔG of reactions increased with the increasing of temperature, too. And ΔG of hydrogen-abstraction reactions induced by $R3^*$ and $R4^*$ are positive, therefore, $R3^*$ and $R4^*$ cannot induce the graft polymerization spontaneously. For $R2^*$, all the reactions with positive ΔG were found with $C_{154}-H_{159}^*$, $C_{164}-H_{163}^*$ and $C_{165}-H_{169}^*$ which locate in epoxy group. In addition, ΔG of H_{159} -abstraction reactions induced by $R1^*$ change from negative to positive, with the increasing of temperature.

Therefore, aromatic radicals ($R1^*$ and $R2^*$) are more favorable than azo ones ($R3^*$ and $R4^*$) for hydrogen-abstraction, and the potential position located between epoxy and phenyl ether groups can be graft sites when induced by proper free radicals, while some of the other positions located in epoxy groups can also be graft sites when induced by proper radicals at appropriate temperature.

C—H bond length and dissociation energy of the potential graft sites

As mentioned above, besides the reported graft sites, some new ones were found. In order to simply compare the difficulty level of hydrogen-abstraction of potential graft sites with that of the reported ones, C—H bond length and dissociation energy of potential graft sites were calculated. The computations of C—H bond length were conducted on simplified structure representatives of the potential graft sites (see Fig. 6).

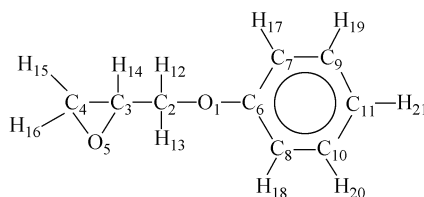


Fig. 6 Model compound of epoxy resin containing the potential graft sites

Table 4. ΔG of hydrogen-abstraction reactions of potential graft sites

ER*	T	R1*	R2*	R3*	R4*	ER*	T	R1*	R2*	R3*	R4*
$C_{153}-H_{156}^*$	298	-0.16	-0.02	0.74	0.90	$C_{164}-H_{163}^*$	298	-0.13	0.01	0.77	0.93
	303	-0.16	-0.02	0.74	0.90		303	-0.13	0.01	0.77	0.93
	333	-0.16	-0.02	0.75	0.90		333	-0.13	0.01	0.78	0.93
	363	-0.16	-0.02	0.75	0.91		363	-0.13	0.01	0.78	0.94
	393	-0.16	-0.02	0.76	0.91		393	-0.13	0.00	0.79	0.94
$C_{153}-H_{157}^*$	423	-0.15	-0.03	0.77	0.92	$C_{164}-H_{167}^*$	423	-0.13	0.00	0.79	0.94
	298	-0.14	0.00	0.76	0.92		298	-0.15	-0.01	0.75	0.91
	303	-0.14	0.00	0.77	0.92		303	-0.15	-0.01	0.75	0.91
	333	-0.14	0.00	0.77	0.93		333	-0.15	-0.01	0.76	0.91
	363	-0.13	0.00	0.78	0.93		363	-0.15	-0.02	0.76	0.92
$C_{154}-H_{159}^*$	393	-0.13	0.00	0.78	0.93	$C_{165}-H_{169}^*$	393	-0.15	-0.02	0.77	0.92
	423	-0.13	0.00	0.79	0.94		423	-0.15	-0.02	0.77	0.92
	298	-0.04	0.10	0.87	1.02		298	-0.12	0.02	0.78	0.94
	303	-0.03	0.10	0.87	1.02		303	-0.12	0.02	0.78	0.94
	333	-0.02	0.11	0.89	1.04		333	-0.12	0.02	0.79	0.94
$C_{158}-H_{161}^*$	363	0.00	0.13	0.91	1.06	$C_{168}-H_{171}^*$	363	-0.12	0.01	0.79	0.95
	393	0.01	0.14	0.93	1.08		393	-0.12	0.01	0.80	0.95
	423	0.03	0.16	0.95	1.10		423	-0.12	0.01	0.80	0.95
	298	-0.64	-0.50	0.26	0.42		298	-0.66	-0.52	0.24	0.40
	303	-0.64	-0.50	0.26	0.42		303	-0.66	-0.52	0.25	0.40
$C_{158}-H_{162}^*$	333	-0.64	-0.51	0.27	0.42	$C_{168}-H_{172}^*$	333	-0.66	-0.52	0.25	0.40
	363	-0.64	-0.51	0.27	0.42		363	-0.66	-0.53	0.25	0.41
	393	-0.65	-0.52	0.27	0.42		393	-0.66	-0.53	0.26	0.41
	423	-0.65	-0.52	0.27	0.42		423	-0.66	-0.53	0.26	0.41
	298	-0.86	-0.72	0.04	0.20		298	-0.67	-0.53	0.23	0.39
$C_{158}-H_{162}^*$	303	-0.86	-0.73	0.04	0.20		303	-0.67	-0.53	0.24	0.39
	333	-0.87	-0.74	0.04	0.19		333	-0.67	-0.53	0.24	0.39
	363	-0.88	-0.75	0.03	0.18		363	-0.67	-0.54	0.24	0.40
	393	-0.89	-0.76	0.02	0.17		393	-0.67	-0.54	0.25	0.40
	423	-0.90	-0.77	0.02	0.17		423	-0.67	-0.54	0.25	0.40

All the values of temperature are in K and energies are in eV.

All the aliphatic C—H bond lengths of potential graft sites in the model compound are listed in Table 5. As can be seen, the C—H bond lengths follow the order, $C_2-H_{12} > C_2-H_{13} > C_3-H_{14} = C_4-H_{15} > C_4-H_{16}$. Bond lengths of C_2-H_{12} , C_2-H_{13} which bonded with epoxy and phenyl ether groups are in the reference range of 0.1096–0.1101 nm mentioned above, while the others are under this reference range.

Table 5. C—H bond length of model compound containing potential graft sites

Bonds	Bond length (nm)	Bonds	Bond length (nm)
C_2-H_{12}	0.1098	C_2-H_{13}	0.1096
C_3-H_{14}	0.1091	C_4-H_{15}	0.1091
C_4-H_{16}	0.1090		

In addition, the C—H bond dissociation energies of potential graft sites were calculated and listed in Table 6. As can be seen, the C—H bond dissociation energies follow the order, $C_{168}-H_{171} < C_{168}-H_{172} < C_{158}-H_{162} < C_{158}-H_{161} < C_{154}-H_{159} < C_{153}-H_{156} < C_{164}-H_{167} < C_{153}-H_{157} < C_{164}-H_{163} < C_{165}-H_{169}$, and bond dissociation energies of $C_{158}-H_{161}$, $C_{158}-H_{162}$, $C_{168}-H_{171}$, $C_{168}-H_{172}$ which bonded with epoxy and phenyl ether groups are under the reference range of 3.8371–4.0127 eV, while the others are slightly beyond the reference range.

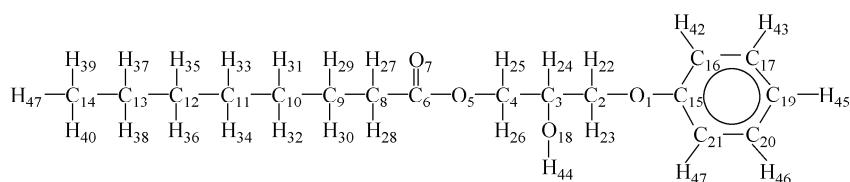
Table 6. C—H bond dissociation energies of potential graft sites

Bonds	BDE (eV)	Bonds	BDE (eV)	Bonds	BDE (eV)
C ₁₅₃ —H ₁₅₆	4.26	C ₁₅₃ —H ₁₅₇	4.28	C ₁₅₄ —H ₁₅₉	4.24
C ₁₅₈ —H ₁₆₁	3.81	C ₁₅₈ —H ₁₆₂	3.66	C ₁₆₄ —H ₁₆₃	4.30
C ₁₆₄ —H ₁₆₇	4.28	C ₁₆₅ —H ₁₆₉	4.32	C ₁₆₈ —H ₁₇₁	3.76
C ₁₆₈ —H ₁₇₂	3.77				

Longer C—H bond length and smaller bond dissociation energy predict that the hydrogen will be slightly more likely to be abstracted. Therefore, the aliphatic secondary hydrogens bonded with phenyl ether and epoxy group are more likely to be abstracted than the reported ones by the same free radical, while the other potential ones are less likely.

Modification for Increasing Graft Sites

As mentioned above, the increase of C—H bond length predicts that hydrogen will be more likely to be abstracted, therefore this effect can be used to increase the number of graft sites by modification of epoxy resin. The simplest modification is the reaction of epoxy resin with aliphatic acid which has longer C—H bonds. The model compound structure of epoxy resin modified with *n*-caprylic acid is shown in Fig. 7 and its C—H bond lengths were calculated and listed in Table 7.

**Fig. 7** Model of modified epoxy resin**Table 7.** C—H bond length of modified epoxy resin model

Bonds	Bond length (nm)	Bonds	Bond length (nm)
C ₂ —H ₂₂	0.1098	C ₂ —H ₂₃	0.1099
C ₃ —H ₂₄	0.1102	C ₄ —H ₂₅	0.1095
C ₄ —H ₂₆	0.1092	C ₈ —H ₂₇	0.1098
C ₈ —H ₂₈	0.1099	C ₉ —H ₂₉	0.1097
C ₉ —H ₃₀	0.1097	C ₁₀ —H ₃₁	0.1100
C ₁₀ —H ₃₂	0.1100	C ₁₁ —H ₃₃	0.1100
C ₁₁ —H ₃₄	0.1100	C ₁₂ —H ₃₅	0.1100
C ₁₂ —H ₃₆	0.1100	C ₁₃ —H ₃₇	0.1099
C ₁₃ —H ₃₈	0.1099	C ₁₄ —H ₃₉	0.1096
C ₁₄ —H ₄₀	0.1097	C ₁₄ —H ₄₁	0.1097
C ₁₆ —H ₄₂	0.1084	C ₁₇ —H ₄₃	0.1087
C ₁₉ —H ₄₅	0.1086	C ₂₀ —H ₄₆	0.1087
C ₂₁ —H ₄₇	0.1086		

It can be seen from Table 7 that, there are some C—H bonds having bond lengths in or beyond the reference range of 0.1096–0.1101 nm, and these longer C—H bonds are located in the alkyl chain of *n*-caprylic acid. The longer C—H bond length indicates the easier hydrogen abstraction, so the aliphatic acid modified epoxy resin will have more grafting sites.

CONCLUSIONS

For the free-radical-induced graft copolymerization of the bisphenol A type epoxy resin, the graft sites found experimentally are favorable according to the Gibbs free energy criterion of the second law of thermodynamics. In addition to these reaction sites, grafting may also take place at other aliphatic carbon atoms of the epoxy resin molecule. Modification of epoxy resins through esterification with aliphatic acid will bring in an increase in the number of graft sites.

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