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Notes

Hyperbranched Poly[allyl ether-*alt*-maleic anhydride] Produced by the Self-Condensing Alternating Copolymerization Approach

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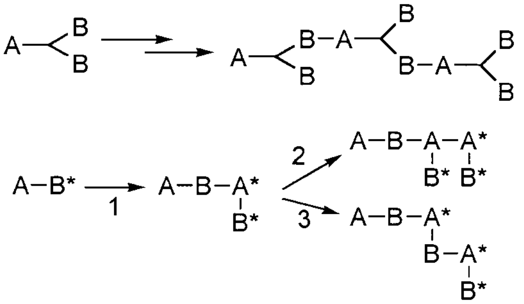
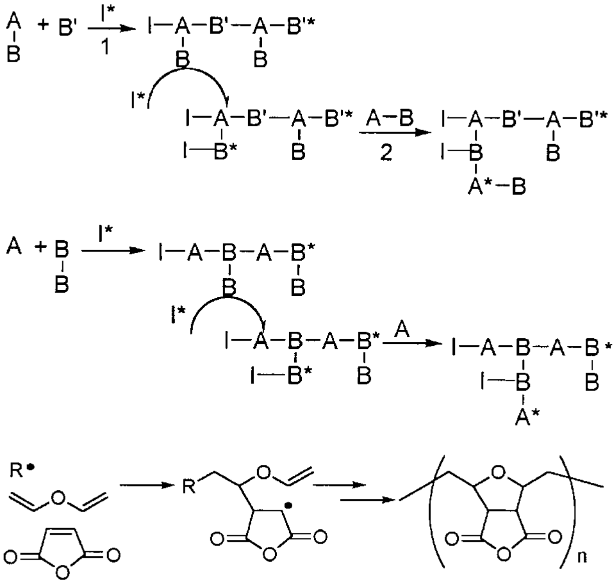
The structures of dendrimers and hyperbranched polymers have lately garnered interest from both academic and industrial viewpoints. However, because the synthesis of dendrimers is far from trivial and requires multistep syntheses, their commercial use has still been very limited. As a consequence of this and other considerations, new methodologies for one-pot reactions to hyperbranched polymers are becoming an increasingly important theme in polymer science. Accordingly, it is very challenging and meaningful work to design new mechanisms and monomer systems that permit the facile synthesis of highly branched polymers. Flory's pioneering work in early 1952 already envisioned that this type of highly branched polymer could be generated by polycondensation of AB_x ($x > 1$) type monomers, in which two types of groups A and B can only in an alternating fashion react with each other (Scheme 1a).[1] Nonetheless, intentional manifestation of hyperbranched polymers had not yet been demonstrated by then. However, it inspired and laid the conceptual foundation for many subsequent research workers in this field. More recently, another intriguing concept of producing hyperbranched polymers by "self-condensing vinyl polymerization" (SCVP) has been introduced by Fréchet et al.[2] and further developed by Hawker[3] and Gaynor[4] et al. The SCVP method greatly further enlarged the availability of monomers and the scope for building polymers with a highly branched architecture. The SCVP approach utilizes AB* type monomers also referred to as "inimers",[5] where A denotes a double bond and B* is a functional group that by external stimulus can be transformed into an initiating moiety for the vinyl groups. Consequently, two kinds of reactions are involved in the SCVP reaction of an AB* monomer: vinyl polymerization of group A to yield at least dimer and self-condensing reaction between B* and A to form a link (1 and 3, Scheme 1b). The function of the pivotal vinyl polymerization step is to multiply the functionality for branching, which in this case does not involve B groups (2 in Scheme 1b). As outlined in Scheme 1b, this versatile SCVP process harnesses the iteration of vinyl polymerization of A and self-condensing reactions between B* and A to yield hyperbranched polymers. However, if either the vinyl polymerization or the self-condensing reaction is strongly favored, mainly linear polymers will only be obtained.[5,6] Furthermore, reactions between active moieties of A* and B* themselves or each other to form links should be avoided or controlled to prevent the polymer from becoming a gel or highly cross-linked material that is insoluble in all organic solvents.

Scheme 1



Scheme 2



In our previous paper, we described a new self-condensing alternating copolymerization approach to hyperbranched polymers from the AB/B′ (allyloxy maleic acid/maleic anhydride) system, in which vinyl group A can only alternately polymerize with vinyl groups B and B′.[7] The monomer B′ is designed to propagate vinyl polymerization of A (1 in Scheme 2a, I* is initiator radical or any other radical). When B is activated, only A can react with it to form a link; i.e., self-condensing reaction between A and B (2 in Scheme 2a) will take place. Therefore, any chain growing from A or B brings branching sites for further branching whereby branches-upon-branches structures will ultimately be formed, and in this manner the foundation has been laid for growth

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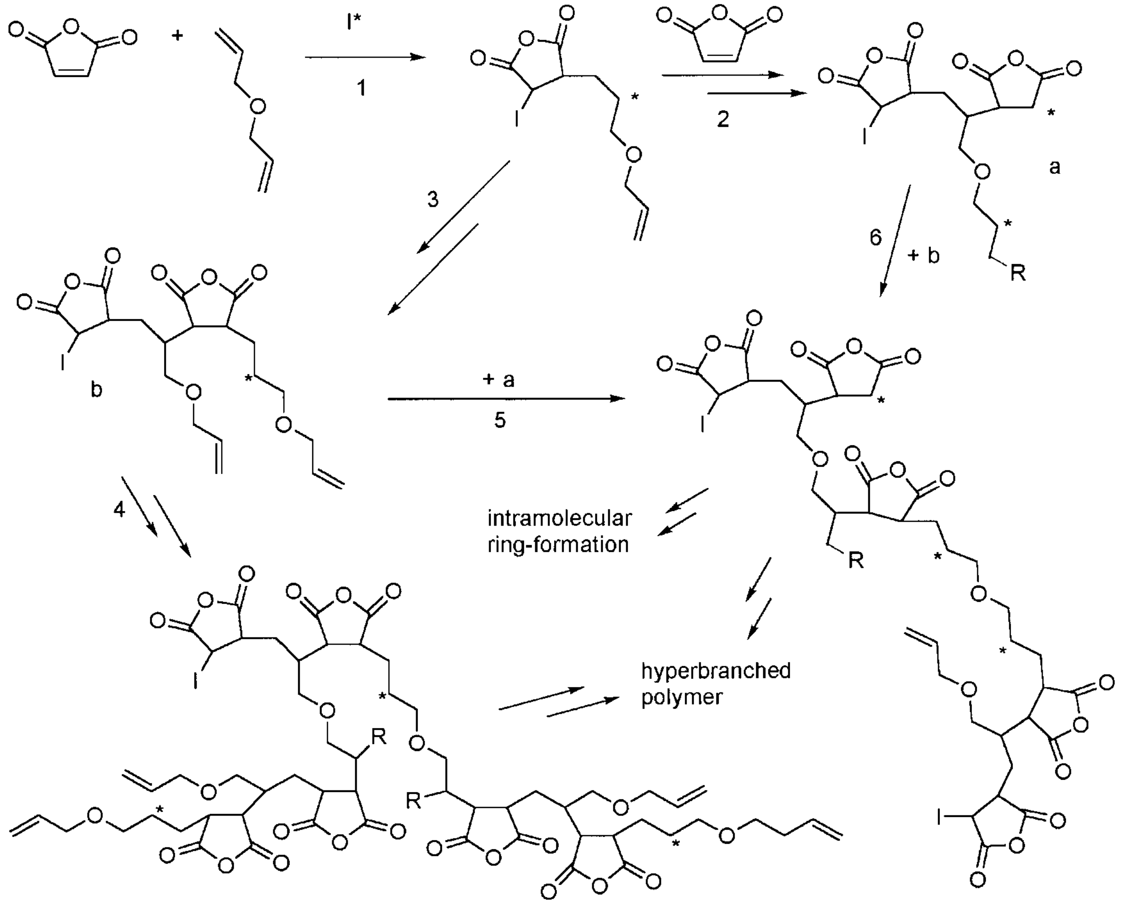
Scheme 3



R: hydrogen or initiator residues.
I: initiator residues.

of highly branched structures with an alternating sequence of monomer units.

According to our previous study,[7] the self-condensing alternating copolymerization reaction should preferably be performed in polar media to maintain a homogeneous system which is helpful for avoiding gelation. Furthermore, it can be noted that the combination termination, which would lead to cross-linking, is also effectively suppressed by hyperbranched radicals containing partial charges. As an added precaution, to prevent gelling and to avoid the macromolecules from growing too large to be supported by solvents in the very late stages of copolymerization is to perform the copolymerization under conditions where A is exhausted and/or concentration controlled.[7] The produced hyperbranched polymer obtained from self-condensing alternating copolymerization of allyloxy maleic acid/maleic anhydride system adopts a globular shape in good solvents, as suggested by our investigations of the condensation reaction between the hyperbranched polymer and diglycidyl ether bisphenol A type epoxy resins.[8]

In this work, we have implemented the self-condensing alternating copolymerization process to an A/B_2 (maleic anhydride/allyl ether) system in an attempt to synthesize hyperbranched polymers in one pot from these cheap and commercially available monomers. There are no clear definition or ways to make a distinction between vinyl polymerization and self-condensing reaction in this A/B_2 system, because all of the reactions shown in Scheme 2b have the characteristics of both vinyl polymerization and self-condensing reaction. Any chain growing from A or B brings branching sites for further branching. In general, this system may have a higher possibility of intramolecular ring closure or cross-linking than that of the AB/B' system, because of the same reactivity of the two vinyl groups of B_2. On the other hand, the branching degree is very likely higher than that of the AB/B' system. The possibility of cyclo-copolymerization to produce linear polymers should also be considered, since for example divinyl ether and maleic anhydride will form five-membered rings (Scheme 2c).[9] However, the allyl ether–maleic anhydride system will give rise to seven-membered rings, which are not thermodynamically favored in ring-formation reactions as is well documented in the chemical literature.

The copolymerization was carried out at 50 °C in acetone,[10] since tetrahydrofuran (THF) was found to be a poor solvent for the allyl ether–MA copolymers at 50 °C. As expected, the systems with an allyl ether–MA molar ratio of 0.5 were highly susceptible to cross-linking, which in turn suggests that cyclo-copolymerization does not take place to any great extent (see Table 1). The vertical dotted line in Figure 1 exhibits the time until gelling occurs for poly(allyl ether-*alt*-MA) hyperbranched polymers prepared using an allyl ether–MA molar ratio of 0.5 (runs 1–9 in Table 1). If the molar ratio of the monomers allyl ether to maleic anhydride was increased to 1 (runs 10 and 11 in Table 1) from 0.5 (runs 1–9 in Table 1), no gelling could be observed

Table 1. Results of Copolymerization of Allyl Ether (AE)−Maleic Anhydride (MA) at 50 °C in Acetone Using BPO as Initiator

no.	AE/MA (mol/mol)	BPO concn (mol % of vinyl groups)	time (h)	yield (wt %)	M_w/MWD[a]
1	0.5	0.61	6.7	4.29	n.d
2	0.5	0.61	7.7	5.15	n.d
3	0.5	0.61	8.7	6.05	n.d
4	0.5	0.61	9.7	6.56	n.d
5	0.5	0.61	11.7	7.77	10000/1.65^a
6	0.5	0.61	13	8.07	n.d
7	0.5	0.61	14	9.37	10500/1.78^a
8	0.5	0.61	15	9.22	13200/1.48^a
9	0.5	0.61	16	*c*	
10[b]	1	2.43	19	13.9	n.d
11[b]	1	2.43	48	53.4	6100/1.58^a 4700/1.42^m
12	1	2.45	24	21.52	10000/1.74^m
13	1	4.85	24	24.19	11200/1.87^m
14	1	8.8	24	43.81	10300/1.92^m

[a] Weight-average molecular weight (M_w) and molecular weight distribution (MWD) were obtained by GPC using polystyrene standards. The GPC data marked with a superscript “m” were obtained from their methylated esters (accomplished by refluxing with methanol), and those marked with a superscript “a” were from their allylated esters (accomplished by reaction with allyl alcohol in the presence of trace of 4-(dimethylamino)pyridine). [b] 73 wt % acetone was used in the system; all other systems used 50 wt % acetone. [c] Cross-linked.

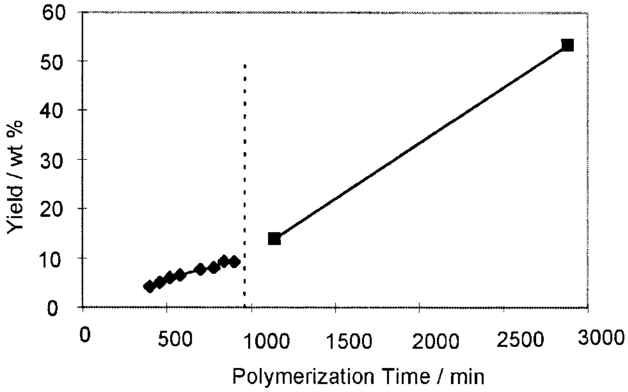


Figure 1. Yields of polymers obtained from runs 1−9 (◆) and runs 10 and 11 (■) in Table 1. The vertical dotted line exhibits the gelling time of the system with an allyl ether−MA molar ratio of 0.5.

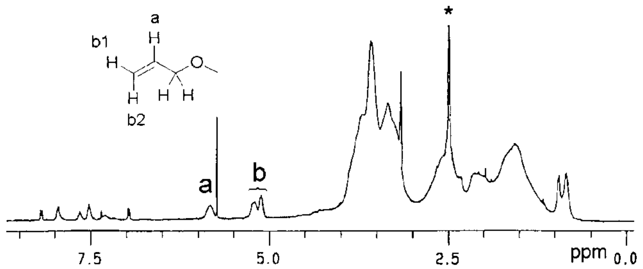


Figure 2. The 400 M Hz ^{1}H NMR spectrum of methylated (allyl ether−maleic anhydride) copolymer obtained from run 12 in Table 1. The peak marked with an asterisk arises from the solvent d_6-DMSO.

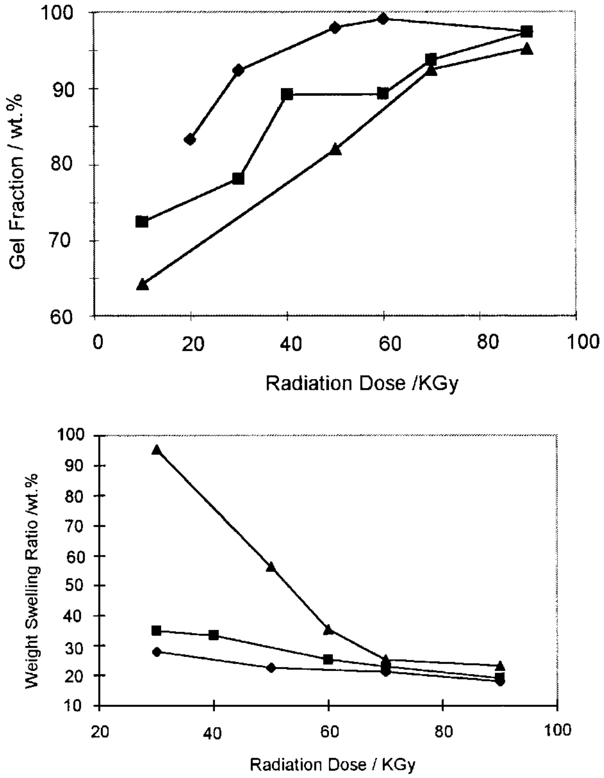


Figure 3. Dependence of gel fractions (a) and swelling degrees (b) of the cross-linked films on radiation doses: ◆, with allylated polymers; ■, with methylated polymers; ▲, without cross-linkers.

within the range of experimental conditions used in this study, i.e., within 2 days of copolymerization. In addition, the molar excess of allylic groups to MA increased the amount of unreacted allylic groups branches in the synthesized hyperbranched polymers, and at the same time the yield of soluble polymers was also greatly increased. The basic mechanism of copolymerization of allyl ether with MA to yield hyperbranched polymers is outlined in Scheme 3. It is obvious from Scheme 3 that keeping the molar ratio of allyl ether to MA equal to 1 or above greatly enhances the likelihood for obtaining hyperbranched polymers with allylic end groups. According to the process described above, when one MA molecule reacts with one allyl ether molecule to form a link, then one allylic group is left as a pendent unreacted branch. The formed allylic branch can either grow new branches by reinitiating chain transfer or take part in the propagating process of another chain. Neither allylic groups nor maleic anhydrides can react with themselves, which markedly decrease the cross-linking possibility. Condensation between macromolecular intermediates does not necessarily result in cross-linking if the condensation process is stopped prior to the event that a finite and very high molecular weight is reached. The copolymerization rate enhances as well as the yields as the concentration of initiator is increased (runs 12−14).

The ^{1}H NMR spectrum of the poly(allyl ether-*alt*-MA) copolymer is shown in Figure 2. The signals marked with a and b at 5.2 and 5.8 ppm arise from the vinylic protons denoted as a and b. (In the ^{1}H NMR spectrum of linear poly(allyl ethyl ether-*alt*-MA) used as reference, the peaks of a and b have completely disappeared.) The molar concentrations of allylic groups in the copolymers of runs 12 and 14 were determined to be 65 and 53 mmol/100 g, respectively, by comparison of the integration of the signals from the allylic groups in the copolymers to those of allyl ether.[8] Thus, in samples of runs 12 and 14 there seems to be approximately 5−7 allylic groups per polymer molecule on average. This result is also further proof that the polymers obtained are hyperbranched polymers and not linear polymers produced by means of cyclopolymerization. In addition, analysis of initiator residues arising from benzoic peroxide (BPO) by the ^{1}H NMR spectrum reveals that there are approximately 2−3 initiator residues (benzene moieties) in one polymer molecule. These results correlate with the assumption that multiple initiating occurs besides chain transfer to growing new branches.

The curing performance of the hyperbranched poly(allyl ether-*alt*-MA) copolymers was investigated in combination with poly(butyl acrylate) by way of electron beam radiation induced cross-linking.[11] As can be seen in Figure 3, a marked difference was observed in curing efficiency between the hyperbranched polymers and the reference poly(butyl acrylate) formulation without external cross-linker; i.e., as could be anticipated, the hyperbranched polymers greatly decrease the radiation dosage required for considerable cross-linking.

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References and Notes

(1) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718.
(2) Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080.
(3) Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763.
(4) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079.
(5) Müller, A. H. E.; Yan, D.; Wulkow, M. *Macromolecules* **1997**, *30*, 7015.
(6) Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A* **1998**, *36*, 955.
(7) Liu, H.; Näsman, J. H.; Skrifvars, M. *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 3074.
(8) Liu, H.; Wilén, C.-E.; Skrifvars, M. *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 4457.
(9) (a) Butler, G. B.; Ingley, F. L. *J. Am. Chem. Soc.* **1951**, *73*, 895. (b) Butler, G. B. *Cyclopolymerization and Cyclocopolymerization*; Marcel Dekker: New York, 1992. (c) Butler, G. B. *Acc. Chem. Res.* **1982**, *15*, 370.
(10) The solutions of allyl ether (Aldrich, 99%), maleic anhydride (Acros, 99%), and benzoyl peroxide (BPO, recrystallized) in dry acetone were sealed in 10 mL ampules and heated to 50 °C. The final production mixtures were cooled and poured into 200 mL 2/1 (v/v) benzene/hexane mixtures. The precipitates were washed several times with chloroform and then vacuum-dried. The final polymers were transformed into their methylated or allylated polymers by reactions with methanol or allyl alcohol, respectively. When reacted with allyl alcohol, solutions of THF were used.
(11) The acetone solutions of poly(butyl acrylate) (self-synthesized, with weight-average molecular weight of 664 000 g/mol) and 8 wt % of the methylated or allylated hyperbranched polymer (obtained from run 12) were applied onto aluminum films to form coatings with a thickness of 0.3−0.5 mm. Poly(butyl acrylate) coating without the hyperbranched polymers were also produced with the same thickness for comparison. The polymer films were irradiated using an electron curtain electron accelerator (Energy Sciences Inc.). Irradiation was carried out under nitrogen atmosphere at an acceleration voltage of 175 kV. The gel fractions and swelling degrees of the coating films were measured in THF.

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