Novel multifunctional hyperbranched polymeric photoinitiators with built-in amine coinitiators for UV curing[†]

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A new class of hyperbranched polymeric photoinitiators with built-in amine coinitiators has been developed, showing high functionality, low viscosity, good compatibility with the usual radiation curable formulations, high photoactivity and low extractability from the cured sample.

Crosslinked polymers derived from photopolymerization are important for a broad variety of applications, such as photocurable coatings, varnishes, lacquers, optical discs, electronic circuits, printing inks and adhesives.^{1,2} For all applications, a photoinitiator system with high photoactivity, good solubility in the curable medium, low odor and toxicity, no darkening deriving from the presence of migratory residues in the network and good storage stability is desired. To satisfy most of the aforementioned requirements, one possible strategy is the synthesis of polymeric photoinitiators by incorporation of the low molecular weight photoinitiator into the main or side chain of polymers.^{3–10}

In radiation-curable formulations, polymeric photoinitiating systems with high functionality and low viscosity are preferred. To date, nearly all known polymeric photoinitiating systems are based on conventional linear polymer structures. For such topologies, an enhancement of the functionality is usually accompanied by an increase of the molecular weight. This, however, enhances the viscosity of the radiation-curable formulations significantly.³

Hyperbranched polymers and dendrimers combine high functionality with low viscosity,^{11–14} in contrast to linear polymers. To date, reports on polymeric photoinitiating systems derived from dendrimers^{15,16} or hyperbranched polymers^{17,18} are very scarce. Herein, we report new, conveniently manufactured hyperbranched polymeric photoinitiators (PPIC) with built-in amine coinitiators which possess the following advantages: (1) high functionality; (2) good compatibility with the usual radiation-curable formulations; (3) low viscosity; (4) high photoactivity; (5) low extractability from the cured sample.

Transparent, yellowish hyperbranched polyglycerols (PG) with an average of 17, 33, 83 and 179 hydroxyl end-groups, were used as scaffolds for the syntheses of multifunctional hyperbranched PPICs. Benzophenone (BP) has been widely used as a Norrish type II photoinitiator due to its low cost, good solubility, good activity and low yellowing on cure. Therefore, it was selected for incorporation into the PPICs as the photoactive moiety. Aromatic and aliphatic tertiary amines, 4-dimethylaminobenzoate (DMB) and 1-piperidinepropionate (PP), were incorporated as coinitiator structures. Since the PPICs with solely BP and DMB or PP functional groups exhibited poor solubility in the usual monomers dipropylene glycol diacrylate (DPGDA) and trimethy-lolpropane triacrylate (TMPTA), compatibilizing groups, such as 2-[2-(2-methoxyethoxy)ethoxy] acetate (MEEA), were introduced to enhance their solubility in the radiation-curable formulations.

For the synthesis of hyperbranched PPICs with aromatic tertiary amine DMB as coinitiator, the inexpensive raw material 4-dimethylaminobenzoic acid was used. The acid-catalyzed direct condensation between PG and 4-dimethylaminobenzoic acid in toluene failed. Subsequently, the 1,1'-carbonyldiimidazole (CDI)-activated carboxylic acid method was employed, as shown in Scheme 1. First PG was partially modified with MEEA under acid-catalyzed condensation conditions. The material obtained was soluble in low boiling point solvents, such as THF and chloroform. Subsequently the CDI-activated 4-dimethylaminobenzoic acid reacted with partially MEEA-modified PG in THF, and the residual hydroxyl groups were modified by CDI-activated (4-benzoylphenoxy)acetic acid.

Compared to the PPICs with an aromatic tertiary amine coinitiator, the synthesis of the PPIC with aliphatic tertiary amine PP coinitiator is more simple (Scheme 2) and can be conducted in one pot, using the acid-catalyzed direct condensation between PG and the other raw materials with carboxylic acid groups.

All resulting PPICs were characterized by ¹H NMR (ESI,[†] Fig. S1 and S2) and FTIR spectroscopy, confirming the successful incorporation of the functional groups into PG. Subsequently, the average degree of substitution with BP, DMB, PP and MEEA moieties can be calculated and the results are compiled in Table 1. The molar ratio of initiator and coinitiator moieties in the resulting PPICs is around 1 : 1, just as expected. The total functionality of initiator plus coinitiator moieties is around 60%, slightly less than the targeted 66%. The average functionality of initiator plus coinitiator moieties in the range of 8 to 106, showing that the obtained PPICs have high functionality.

The resulting PPICs have good solubility in the usual radiationcurable monomers DPGDA and TMPTA. Thus, with the mixture of DPGDA and TMPTA as the monomers six radiation-curable formulations based on the PPICs have been prepared (ESI,† Table S1). For comparison, two formulations with the low molecular weight photoinitiator methyl (4-benzoylphenoxy)acetate (MBPA) and photo-coinitiator 2-ethylhexyl 4-dimethylaminobenzoate (EHA) were also prepared (ESI,† Table S1). The content of

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Scheme 1 Synthesis of hyperbranched polymeric photoinitiator with built-in aromatic tertiary amine coinitiator.

photoinitiator moiety and the photo-coinitiator moiety in all formulations was adjusted to be similar, as shown in Table 2. The photoactivity of the resulting PPICs with aromatic tertiary

amine coinitiator moieties was compared with the corresponding

low molecular weight MBPA photoinitiator and EHA coinitiator mixture. All curing experiments were performed under a nitrogen blanket. The exposure time of all reactive mixtures under the UV lamp was kept constant. The output power of the UV lamp was



Scheme 2 Synthesis of hyperbranched polymeric photoinitiator with built-in aliphatic tertiary amine coinitiator.

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Table 1	Compositions of all	multifunctional	hyperbranched	polymeric	photoinitiators	with built-in	amine coinitiators
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Polymer ^a	Average functionality of the functional moieties in PPIC ^b							
	BP	DMB	PP	MEEA	X ^c	$M_{\rm n} (\times 10^{-3})$	General formula	
PPIC-1	4.8	4.8	0	7.4	17	4.3	PG ₁₇ (BP) _{4.8} (DMB) _{4.8} (MEEA) _{7.4}	
PPIC-2	11.4	9.3	0	12.3	33	8.4	PG33(BP)11.4(DMB)9.3(MEEA)12.3	
PPIC-3	4.3	0	4.6	8.1	17	4.2	PG ₁₇ (BP) _{4.3} (PP) _{4.6} (MEEA) _{8.1}	
PPIC-4	8.2	0	8.9	15.9	33	7.9	$PG_{33}(BP)_{8,2}(PP)_{8,9}(MEEA)_{15,9}$	
PPIC-5	22.7	0	24.8	35.5	83	20.5	PG ₈₃ (BP) _{22.7} (PP) _{24.8} (MEEA) _{35.5}	
PPIC-6	49.0	0	56.7	73.3	179	44.4	PG ₁₇₉ (BP) ₄₉ (PP) _{56.7} (MEEA) _{73.3}	

^{*a*} PPIC: polymeric photoinitiators with built-in amine coinitiators. ^{*b*} BP represents the benzophenone moiety, DMB represents the 4-dimethylaminobenzoate moiety, PP represents 1-piperidinepropionate, MEEA represents the 2-[2-(2-methoxyethoxy)ethoxy] acetate moiety. ^{*c*} X gives the total functionality of the PPIC.

 Table 2
 Comparison of curing speed and viscosity of the radiation-curable formulations based on monomeric and polymeric photoinitiating systems

No. ^a	Photoinitiating system ^b	BP (%)	DMB (%)	PP (%)	MEEA (%)	PMO ^c (%)	Viscosity/mPa s
1	MBPA + EHA	3.7	3.3	0	0	50	26.6
2	MBPA + EHA	3.7	4.1	0	0	50	26.9
3	PPIC-1	3.7	3.3	0	5.5	50	55.5
4	PPIC-2	4.4	3.3	0	4.7	50	69.4
5	PPIC-3	3.3	0	3.1	6.2	50	48.9
6	PPIC-4	3.4	0	3.2	6.5	50	53.4
7	PPIC-5	3.6	0	3.4	5.6	50	54.4
8	PPIC-6	3.6	0	3.6	5.3	50	75.4
^a Radiat	ion-curable standard formulati	on with dipror	oylene glycol diac	rvlate and trim	ethylolpropane tria	crylate as monom	ners. ^b MBPA is the
low m	olecular photoinitiator mo	ethyl (4-benz	oylphenoxy)aceta	te; EHA i	s the monome	ric photo-coinit	iator 2-ethylhexyl

adjusted to assure that the formulations were fully cured within the same time. A sample was considered as fully cured when scratching with a Q-tip caused no visual damage, which is a simple standard test. The percentage of maximum output (PMO) of the UV lamp was taken as a measure for the curing speed. The lower this number was, the higher the curing speed. Comparing the PMO data listed in Table 2, it is obvious that the curing speed of the formulations derived from the PPICs (No. 3 and 4 in Table 2) was the same as those of the formulations derived from their corresponding low molecular weight analogues (No. 1 and 2 in Table 2). From Table 2 it is also obvious that the type of coinitiator moiety and the molecular weight of the respective PPICs does not affect the photoactivity.

Low viscosity is preferred in nearly all radiation-curable formulations. Especially for ink-jet application, a significant increase in the solution viscosity has to be avoided to keep the ink jettable. Use of linear polymers usually enhances the viscosity of the radiation-curable formulation significantly.³ In order to keep viscosity low, oligomers with molecular weight most preferably lower than 800 g mol⁻¹ are preferred.¹⁹ In our case, the molecular weight of the PPICs used is much higher than 800 g mol^{-1} , being in the range of 4200 to 44,400 g mol⁻¹. However, compared with the formulations based on the low molecular weight photoinitiator and coinitiator, the viscosity of the formulations based on the subject PPICs did not increase dramatically, being still jettable as inkjet ink. Thus, it can be concluded that the hyperbranched polymers with complex functionalities showed remarkably low viscosity that did not increase significantly with molecular weight. This phenomenon is characteristic of compact spheroidal structures, present in both dendritic polymers^{20–22} and star polymers.^{23,24}

Low extractability in the cured samples is preferred, since the extractable low molecular weight residues remain mobile and can deteriorate the physical properties of the packaging materials. Moreover, in food packaging printed with such radiation-curable compositions the low molecular weight residues might be extracted into the packaged food. Thus, we also measured the low molecular weight residue extractability of the PPIC samples and found that the extracted amount was lower than the detection limit of the methods used to accurately determine the extracted amounts, which means that the extracted amount of residues is clearly below 50 mg m⁻². This illustrates that almost no photoreactive residues can be extracted from the cured samples, in contrast to the completely extracted photoinitiator residues for the low molecular weight photoinitiator MBPA, and around 30% for the hyperbranched polymeric photoinitiator without tertiary amine coinitiator moieties.²⁵ Thus, it is obvious that the tertiary amine coinitiator moieties improve the permanent fixation of the PPICs in the final polymer network.

In conclusion, new, conveniently manufactured hyperbranched polymeric photoinitiators with built-in amine coinitiators have been developed. The obtained PPICs possessed high functionality, low viscosity, and good compatibility with the usual radiation curable formulations. Furthermore, high photoactivity and almost no extractable low molecular weight residues in the cured sample were observed. Hyperbranched polymeric photoinitiators, such as the ones studied, appear to be promising for further exploration in food packaging applications.

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