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

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Experimental Part

Materials

2-[2-(2-Methoxyethoxy)-ethoxy] acetic acid (MEEAA, tech) and 1-piperidinepropionic acid (PPA, 99%) were purchased from Aldrich and used as received. 4-Dimethylaminobenzoic acid (98%), 1,1'-carbonyldiimidazole (CDI, 97%) and *p*-toluenesulfonic acid monohydrate (99%) were purchased from Acros. Dipropylene glycol diacrylate (DPGDA) was purchased from UCB. Trimethylolpropane triacrylate (TMPTA) was purchased from BASF. 2-Ethylhexyl 4-dimethylamino benzoate (EHA) was purchased from Aceto. Hyperbranched polyglycerol samples with trimethanolpropane (TMP) core: PG_{17} (number-average molecular weight $\overline{M}_n$ =1.21 × 10^3, $\overline{M}_w/\overline{M}_n$ = 1.6), PG_{33} ($\overline{M}_n$ =2.32 × 10^3, $\overline{M}_w/\overline{M}_n$ =2.6), PG_{83} ($\overline{M}_n$ =5.99 × 10^3, $\overline{M}_w/\overline{M}_n$ =2.6), and PG_{179} ($\overline{M}_n$ =1.31 × 10^4, $\overline{M}_w/\overline{M}_n$ =2.9) were prepared as reported previously.[1] The syntheses of (4-benzoylphenoxy)acetic acid (BPAA) and methyl (4-benzoylphenoxy)acetate

(MBPA) were described elsewhere. Poly(ethylene terephthalate) (PET) substrate with an anti-blocking layer having anti-static properties on the backside was available from Agfa Graphics as P125C PLAIN/ABAS.

Abbreviation of the resulting PPIC samples

The resulting PPICs were designated $(X)_y$: **t** represents the average end group number of PG; **X** designates the functional groups attached to PG, which include benzophenone (BP), 2-[2-(2-methoxyethoxy)-ethoxy]acetate (MEEA), 4-dimethylaminobenzoate (DMB) and 1-piperidinepropionate (PP) groups. **y** represents the average functionality of **X** moieties of PG.

Synthesis of multifunctional hyperbranched PPICs with BP, DMB, and MEEA moieties

The synthesis is exemplified for the polymer $\mathbf{PG_{17}(BP)_{4.8}(DMB)_{4.8}(MEEA)_{7.4}}$: The solution of 1.67g (10.0mmol) of 4-dimethylaminobenzoic acid and 1.63 (10.0mmol) of CDI in 20ml of THF was refluxed for 3h. Then it was added to the flask containing 1.44g (1.19mmol) of PG and the mixture was refluxed overnight under vigorous stirring. The solution of 2.07g (8.0mmol) of *BPAA*, 1.23ml (8.0mmol) of MEEAA and 2.61g (16.0 mmol) of CDI in 20ml of THF was stirred at ambient temperature for 1h, and subsequently added to the solution containing PG partially modified with DMB. The mixture was stirred at ambient temperature overnight. Water was added to destroy the residual CDI and CDI activated acid. After removing most of the volatile

components under vacuum, the residue was dissolved in chloroform. The mixture was washed twice with 2N of HCl aq, three times with deionized water, twice with 10% of NaOH aq and several times with NaCl aq until pH=7. After removing the volatile components under vacuum, the residual water was removed by forming an azeotrope with toluene. After filtration, most of the toluene was removed and then the residue was kept at 40^{o} C in vacuum oven overnight. Yield=50%. ^{1}H NMR ($CDCl_3$): δ = 0.77, 1.32 (TMP core of PG); 2.99 (($C\underline{H_3})_2$N-); 3.07-5.52 (protons of PG and MEEA moieties, -OC$\underline{H_2}$COO-); 6.56, 6.92, 7.34-8.02 (protons of aromatic ring of BP and DMB moieties).

Synthesis of multifunctional hyperbranched PPICs with BP, PP and MEEA moieties

The synthesis is exemplified for the polymer, **$PG_{17}(BP)_{4.3}(PP)_{4.6}(MEEA)_{8.1}$:** 2.05g (1.69mmol) of PG_{17}, 2.21g (8.57mmol) of *BPAA*, 1.35g (8.57mmol) of PPA, 1.77ml (11.4mmol) of MEEAA and 2.18g (11.4mmol) of *p*-toluenesulfonic acid monohydrate were added into a 100ml one-neck flask equipped with Dean-Stark and condenser. Then 40ml of toluene was added. The mixture was heated to 136^{o}C and stirred for around 2h. Then 0.88ml (5.7mmol) of MEEAA was introduced. The mixture was stirred under the same conditions for an additional 4h. After removing most of the volatile components under vacuum, the residue was dissolved in chloroform. The mixture was washed twice with 10% of NaOH aq and several times with NaCl aq until pH=7. After removing the volatile components under vacuum, the residual water was removed by forming an azeotrope with toluene. After filtration, most of the

toluene was removed and then the residue was kept at 40° C in vacuum oven overnight. Yield=86%. ^{1}H NMR ($CDCl_3$): δ = 0.77, 1.32 (TMP core of PG); 1.14-1.64 (β and γ $C\underline{H_2}$ in piperidine ring); 1.98 ($C\underline{H_3}COO$-); 2.13-2.66 (α $C\underline{H_2}$ in piperidine ring, -$NC\underline{H_2}C\underline{H_2}COO$-); 2.98-5.42 (protons of PG and MEEA moieties, -$OC\underline{H_2}COO$-); 6.62-8.05 (protons of aromatic ring of BP moieties).

Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 spectrometer, operated at 300 MHz and 75.4 MHz, respectively. FTIR spectra were recorded on a Nicolet 5DXC ATR-FTIR spectrometer. The viscosity of the radiation curable composition was measured with a Brookfield DV-II+ viscometer at 25 °C and shear rate 3RPM. Alltime C18 μm HPLC column (ALLtech, 150mm×3.2mm) was used to analyze the extractant. Fusion DRSE-120 conveyer equipped with a Fusion VPS/1600 lamp (D-bulb) was used for the UV curable process.

The process for radiation curing

The UV curable compositions were coated on an unsubbed 100μm PET substrate using a bar coater and a 10μm wired bar. Each coated layer was cured using a Fusion DRSE-120 conveyer, equipped with a Fusion VPS/1600 lamp (D-bulb), which transported the samples under the UV lamp on a conveyer belt at a speed of 20m/min. A sample was considered as fully cured at the moment scratching with a Q-tip caused

no visual damage. The percentage of the maximum output of the lamp was taken as a measure for the curing speed. The lower the number was, the higher the curing speed.

Method of extraction for photoinitiators and coinitiators

The cured sample (24x31 cm) and the PET overlay were extracted with THF by agitating the sample in a dipping tank filled with THF for 15 minutes. The samples were rinsed with THF and the combined THF-solutions were concentrated to 9 ml. The final volume of the THF-solutions was adjusted to 10 ml. 100µl of this solution was filtered over a 0.45µm PVDF-filter and injected on a 3x mixed B column set and eluted with THF/acetic acid 95/5. A refractive index detector was used. The concentration of extracted photoreactive polymers was estimated using standard solutions of the reference polymers.

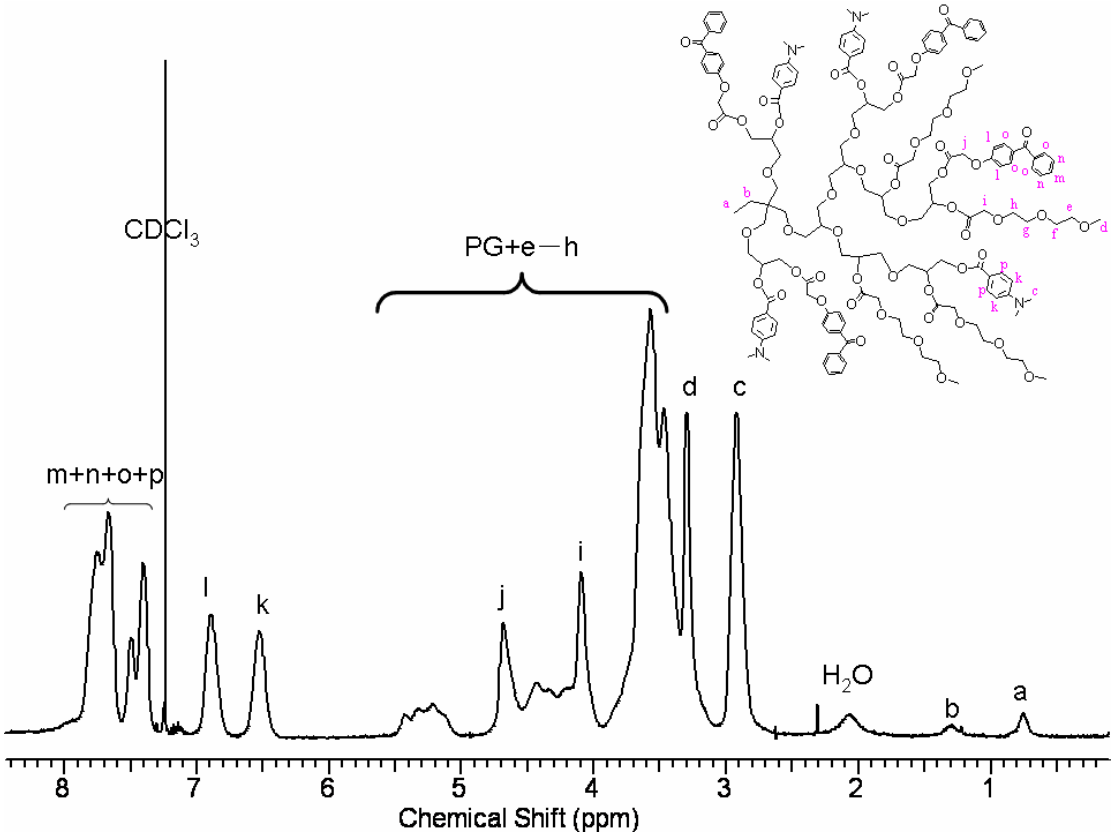

Figure S1. Typical ^{1}H NMR spectrum of multifunctional hyperbranched polymeric photoinitiators with built-in aromatic tertiary amine coinitiators $[PG_{33}(BP)_{11.4}(DMB)_{9.3}\ (MEEA)_{12.3}]$

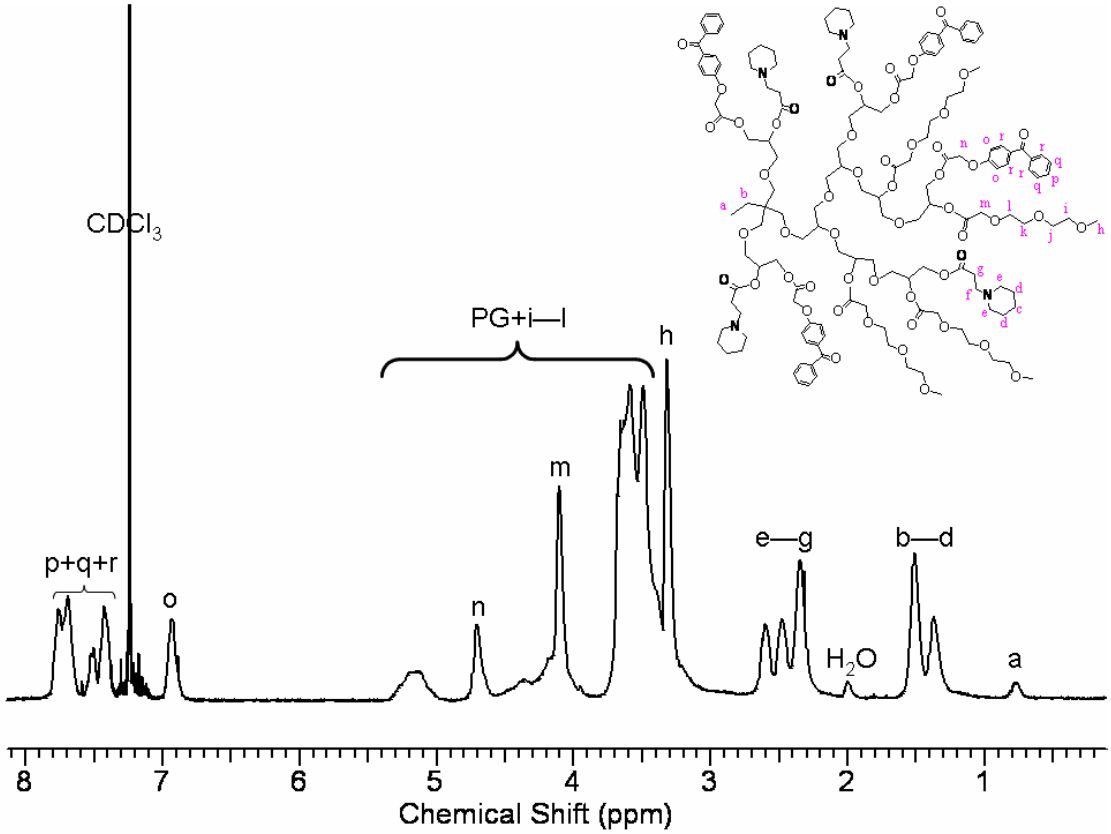

Figure S2. Typical ^{1}H NMR spectrum of multifunctional hyperbranched polymeric photoinitiators with built-in aliphatic tertiary amine coinitiators $[PG_{33}(BP)_{8.2}(PP)_{8.9}(MEEA)_{15.9}]$

Table S1. Radiation-curable formulations based on monomeric and polymeric photoinitiating system

	Composition of radiation-curable formulation (wt%) [a)]										
No.	DPGDA	TMPTA	EHA	MBPA	PPIC-1	PPIC-2	PPIC-3	PPIC-4	PPIC-5	PPIC-6	DBP
1	47.0	40.0	5.5	5.5	—	—	—	—	—	—	2.0
2	45.5	40.0	7.0	5.5	—	—	—	—	—	—	2.0
3	40.0	40.0	—	—	18.0	—	—	—	—	—	2.0
4	40.0	40.0	—	—	—	18.0	—	—	—	—	2.0
5	40.0	40.0	—	—	—	—	18.0	—	—	—	2.0
6	40.0	40.0	—	—	—	—	—	18.0	—	—	2.0
7	40.0	40.0	—	—	—	—	—	—	18.0	—	2.0
8	40.0	40.0	—	—	—	—	—	—	—	18.0	2.0

[a)] DPGDA: dipropylene glycol diacrylate; TMPTA: trimethylolpropane triacrylate; EHA: 2-ethylhexyl 4-dimethylaminobenzoate; MBPA is the monomeric photoinitiator, methyl (4-benzoylphenoxy)acetate; PPICs are polymeric photoinitiators shown in Table 1; DBP: Dibutyl phthalate

[1] A. Sunder, R. Hanselmann, H. Frey, R. Mülhaupt, *Macromolecules* **1999**, *32*, 4240.
[2] M. Aydin, N. Arsu, Y. Yagci, *Macromol. Rapid Commun.* **2003**, *24*, 718.