

Photosensitive polymers

I. Uni- and copolymerization behaviour of 1,3-bis-(4-benzoyl-3-hydroxyphenoxy)-2-propyl methacrylate*

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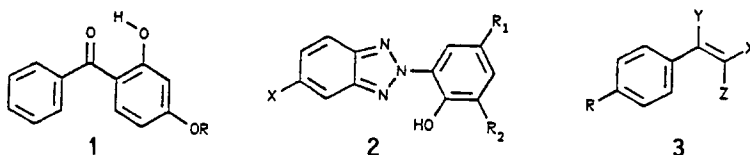
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Summary

The commercially available monomeric UV absorber 1,3-bis-(4-benzoyl-3-hydroxyphenoxy)2-propyl methacrylate readily undergoes radical uni- and copolymerization to yield polymers which are in the chromophore UV absorbing region identical in regard to the monomer. The copolymerization parameters with styrene and MMA, respectively, were determined from ¹H-n.m.r. and GPC measurements.

Introduction

For applicational technical uses most polymers have to be protected against light irradiation by the addition of UV absorbers and antioxidants. Among the UV absorbers, most of the compounds are hydroxybenzophenone **1**, hydroxybenzotriazole **2**, and cinnamic ester **3** derivatives. Many of these compounds have been alkylated in order to increase the solubility in nonpolar polymers such as poly(ethene) or poly(styrene), or polar substituents are attached in order to improve interaction with polymers such as poly(acrylonitrile) or PMMA. But since most of the common stabilizers are of low molar masses, there still is the problem of migration out of the polymer matrix.



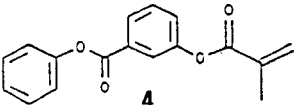
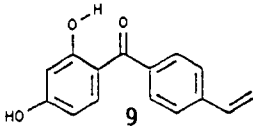
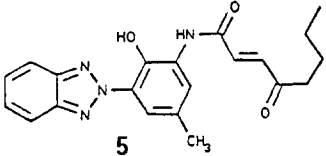
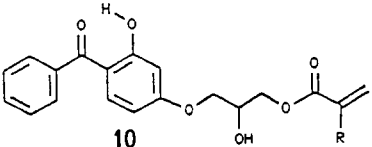
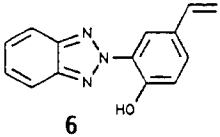
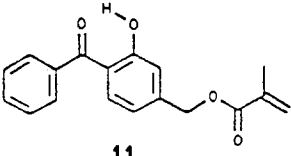
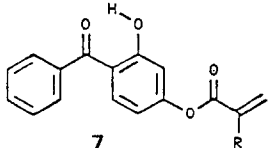
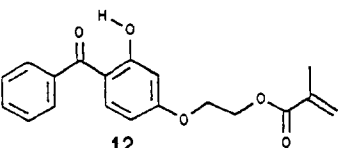
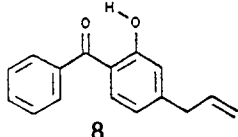
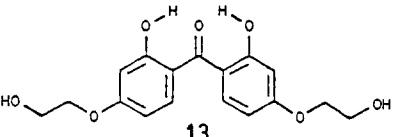
There have already been made attempts to overcome this diffusion problem by incorporating the UV absorbing moieties into polymers in order to improve long time stability. Some examples of UV absorbing Monomers which undergo radical or condensation polymerization reactions are compiled in Tab. 1. Recently radical copolymerization of methacrylic derivatives of hydroxybenzophenone and of tetramethylpiperidine has been published ¹.

*Dedicated cordially to Prof. Dr. Paul Rempp on the occasion of his 60th birthday

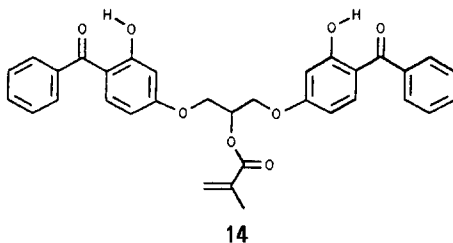
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***Taken in part from the Diploma Thesis of T.S.W., Universität Hannover, 1987

Table 1: UV absorbing monomers, some literature examples

monomer	lit.	monomer	lit.
 4	2	 9	9
 5	3	 10	10
 6	2	 11	11
 7	4-8	 12	12
 8	4	 13	13

We wish here to report on the uni- and copolymerization behaviour of 1,3-bis-(4-benzoyl-3-hydroxyphenoxy)2-propyl methacrylate **14** upon radical initiation.



Results and discussion

Unipolymerization

Surprisingly, in spite of the very bulky substituent to the methacryloyl C=C double bond, monomer **14** readily undergoes radical unipolymerization reactions of different types. The main problem is to separate the polymer properly from monomer since there are only few solvent/nonsolvent systems available. It proved best to add a THF solution of the polymerization product to a mixture of methanol/acetone 2:1 (v:v). After three times of reprecipitation all monomer was removed from the polymer (TLC, CHCl₃/THF, 20:1, v:v). A quantitative detection of residual monomer can be obtained from GPC, Fig. 1. Monomer and polymer peaks are well separated.

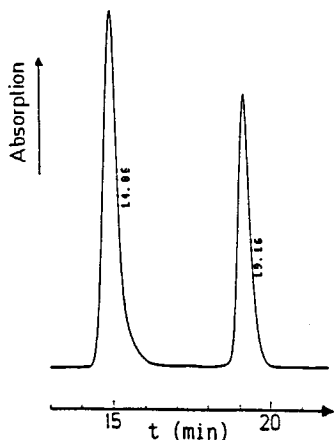


Fig. 1: GPC separation of polymer and monomer **14**

Monomer and polymer **14** show identical UV absorption as is demonstrated in Fig. 2.; no wavelength shifts are observed by converting the chromophore to a polymer.

Because of only small differences in solvent solubility of the polymer in respect to the monomer, attempts to perform a precipitation polymerization were of only minor success. CCl₄ proved to be best but the polymer tends to turn to a rubberlike consistence which makes it necessary to remove the unipolymerized monomer by repeated reprecipitation. After 75 min the conversion from the saturated solution is as high as 80 %; the molar mass is higher in solution polymerization.

At photopolymerization conditions without photoinitiator and performed in a Solidex photoreactor using a mercury high pressure vapour lamp from Philipps (HPK 125 W), conversions were very low even after reaction times as long as 48 hrs.

From emulsion polymerization experiments in which the monomer was dissolved in toluene and then emulsified in water, good polymer yields were obtained. The organic solvent was removed by steam distillation and from the crude collected polymer the remaining monomer detected by GPC. Results are compiled in Tab. 2.

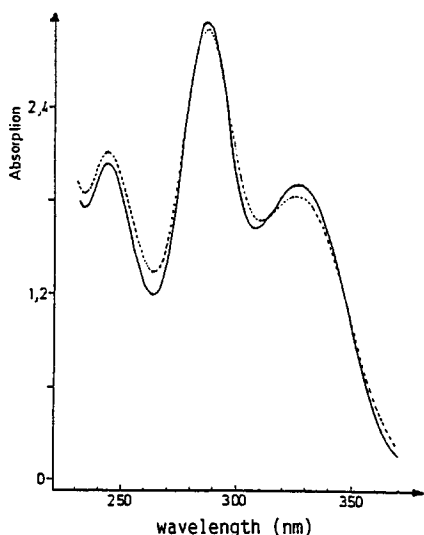


Fig. 2: UV spectra of polymer (---) and monomer (—) **14** in THF; [monomer] = 0,052 g/L, [polymer] = 0,054 g/L, d = 1 cm.

Table 2: Emulsion polymerization of monomer **14**

Entry	Initiator	Emulsifier	Buffer	Reaction time (h)	Yield Polymer (%)	Monomer included (% GPC)
1	$K_2S_2O_8$	+	+	>2	65	1.8
2	$(NH_4)_2S_2O_8$	+	-	7	65	2.7
3	$(NH_4)_2S_2O_8$	-	-	5	93	8.3

reaction temperature: 60°C; N_2 ; 4 g monomer, 50 mL toluene, 100 mL water; [initiator] = 0.003 mole/L; emulsifier: Na-laurylsulfate; buffer: $Na_2H_2PO_4 \cdot 2H_2O$; work up by water steam distillation

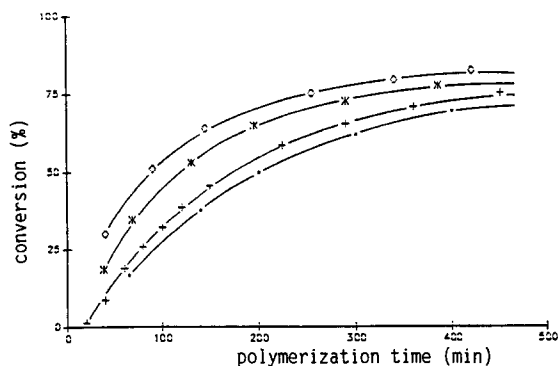


Fig. 3: Solution polymerization of **14**, THF, argon, 60°C; [**14**] = 0.145 mole/L; [AIBN] $\cdot 10^4$ mole/L: \cdot = 2.92; + = 4.87; * = 10.96; \circ = 24.6; conversions were determined by GPC.

In Fig. 3, solution polymerization of monomer **14** in THF acting as solvent runs normally. The curves do not arise from the origin because of warming up the reaction solution before polymerization begins. However, it has been checked independently that no inhibition occurs when polymerization is carried out in small scale experiments.

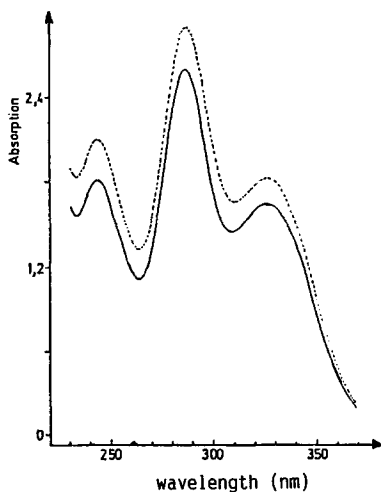
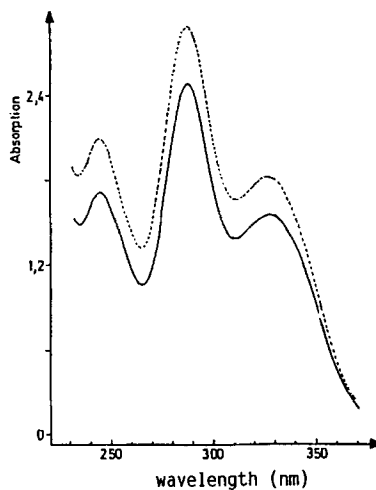
Copolymerization with styrene and with MMA

Both monomers styrene as well as methyl methacrylate copolymerize with monomer **14** to yield random copolymers. In the experiments, copolymer composition was determined from 1H -n.m.r. measurements of the isolated copolymers as well as from GPC analysis of the relative comonomer proportion in the copolymerization mixture. The results differ slightly because of some uncertainties in peak integration, see Tab. 3. For the GPC analysis, styrene and MMA were detected at the absorption maximum at 250 nm, the monomer **14** was registered at 327 nm where styrene and MMA are transparent. The comonomer mixtures were calibrated with the absorptions of the pure monomers at different concentrations.

The copolymerization parameters were calculated from Mayo-Lewis and from Fineman-Ross plots and were also calculated according to Kelen and Tüdös¹⁴, the latter values being collected in Tab. 3. The copolymers are soluble in common organic solvents and show almost the same solution properties as poly(styrene) or PMMA unipolymers. Molar masses from osmosis measurements are in the 200.000 to 300.000 region and confirm a regular radical copolymerization mechanism.

Table 3: Radical copolymerization of monomer **14** with styrene and with MMA

Monomer $M_2 = \text{Styrene}$				Monomer $M_2 = \text{MMA}$			
Entry	X	Y_{nmr}	Y_{gpc}	Entry	X	Y_{nmr}	Y_{gpc}
1	3.62	1.84	1.92	1	4.07	3.63	3.79
2	1.86	1.46	1.47	2	2.10	2.03	1.99
3	0.80	0.9	0.77	3	1.00	1.18	1.08
4	0.44	0.69	0.71	4	0.48	0.65	0.37
5	0.16	0.42	0.30	5	0.20	0.29	0.20
		nmr				gpc	
		r_1	r_2			r_1	r_2
Fineman-Ross		0.27	0.22	0.31	0.34	0.78	0.55
Kelen-Tüdös		0.29	0.25	0.33	0.37	0.82	0.60
$X = [M_1]_0/[M_2]_0$; $Y = m_1/m_2$; 60°C; AIBN; THF; conversion 4-11 %							

Fig.4: UV spectra of poly(**14**) (---) and of poly(**14**-co-styrene) (—) in THFFig.5: UV spectra of poly(**14**) (---) and of poly(**14**-co-MMA) (—) in THF

Here again, in Figs. 4 and 5 the UV spectra of the copolymers of monomer **14** either with styrene or with methyl methacrylate are identical in regard to the unipolymer poly(**14**). An estimation from the r -parameters shows that the composition of the copolymers can be varied widely thus giving the opportunity to change the UV absorber proportion in the copolymers over the whole scale.

Experimental

Monomer **14** was supplied by Riedel-de Haen AG, Seelze, purity 99.0 %, and used without further purification.

Styrene and methyl methacrylate were purified and stored according to the literature ¹⁵.

AiBN as initiator was recrystallized twice from diethyl ether. All solvents were carefully dried and stored under argon.

Solution polymerization and copolymerization reactions were carried out in septum sealed ampoules under argon.

The UV spectra were recorded by means of a Perkin-Elmer Lambda 5 spectrometer.

The ¹H-n.m.r. spectra were recorded on a Bruker WP 80 SY instrument.

Molar masses were determined by membrane osmometry using a Knauer instrument. GPC measurements were performed with a Spectra Physics SP 8100 instrument and a column combination of 50 Å → 100 Å (PL-gel 5 µm) → 100 Å (Waters ultrastyrigel) at 40°C with THF as solvent.

Acknowledgements

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