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Photopolymerization of dimethacrylates in the presence of 2-mercaptobenzothiazole (MBT) and 2,2'-benzothiazole disulfide (BTDS)

RAPID COMMUNICATION

Summary — The effect of a heteroaromatic thiol and disulfide, *viz.* MBT and BTDS, was preliminarily studied in the photopolymerization of tetraethylene and triethylene glycol dimethacrylates (TETGDM, TEGDM), initiated with type I (Irgacure 369) and type II (camphorquinone, CQ) photoinitiators and benzoyl peroxide (BPO) as thermal initiator in air or in Ar. Polymerization was run under 300–400 nm or > 400 nm irradiation (Hg and halogen lamp, resp.) and its kinetics was followed by isothermal DSC [9] (Figs. 1–3). In Ar, the additives had no influence on the Irgacure 369-initiated polymerization of TETGDM; in air, each additive retarded the polymerization and decreased the conversion of double bonds. Retardation of polymerization by additives was also observed, both in air and in Ar, in the process initiated by BPO. In the CQ-initiated polymerization of TEGDM the additives accelerated the polymerization. In air, BTDS raised the maximum polymerization rate to a value somewhat lower than did MBT, and did not reduce the induction period. In Ar, BTDS accelerated the polymerization considerably, much more than did MBT. Results are discussed in terms of the hydrogen abstraction and chain transfer reactions and also photochemical reactions of the additives.

Key words: photopolymerization, dimethacrylates, thiols, disulfides, kinetics.

Thiols and disulfides are well-known chain transfer agents [1–6]. In the polymerizing system they give rise to a decrease in the molecular weight of the polymer produced (in linear systems) or to a decrease in the network crosslink density (in crosslinking systems) and suppress the gel effect [2]. Free-radical polymerization in the presence of thiols or disulfides as chain transfer agents has been applied to prepare terminally reactive oligomers [3, 4]. Disulfides are used as photoinitiators [5, 6].

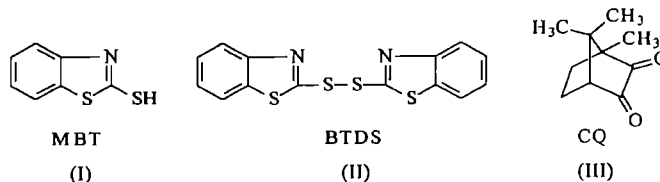
Thiol-ene photocurable systems are less sensitive to oxygen inhibition than is a conventional radical-induced polymerization owing to the ability of peroxy radicals to abstract hydrogen atom from thiols with the formation of initiating radicals RS^{\bullet} [7]. The excited triplet state of benzophenone abstracts hydrogen from thiols and produces thiyl radicals [8]. Thus, thiols may be useful as hydrogen donors in type II photoinitiating systems.

These special properties of thiols and disulfides prompted us to study the influence of a series of hetero-aromatic compounds containing -SH and -S-S- func-

tionality on the photopolymerization of multifunctional (meth)acrylates. This paper presents preliminary results of these investigations.

EXPERIMENTAL

2-Mercaptobenzothiazole (MBT), 2,2'-benzothiazole disulfide (BTDS), camphorquinone (CQ), (tetraethylene glycol) dimethacrylate (TETGDM) and (triethylene glycol) dimethacrylate (TEGDM) were purchased from Aldrich, 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (BDMB, Irgacure 369) from Ciba-Geigy and benzoyl peroxide (BPO) from Merck.



The polymerization kinetics was monitored under isothermal conditions in a high-purity argon atmosphere (< 0.0005% O₂) or in air by a differential scanning calorimeter (DSC 605 M, Unipan-Termal, Warsaw) equipped with a lid specially designed for photochemical measurements. The procedure was the same as that described elsewhere [9]. Polymerization was initiated by 300–400 nm radiation from a Hg medium pressure lamp or from a halogen lamp (> 400 nm).

RESULTS AND DISCUSSION

For the polymerization of TETGDM initiated by BDMB (the photofragmenting initiator) in the presence of MBT and BTDS, the polymerization rate is plotted against irradiation time (Fig. 1). Analysis of the results

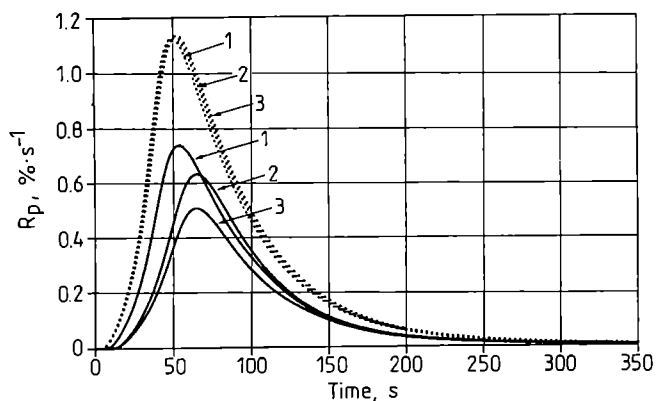
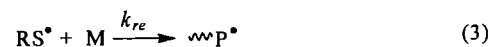
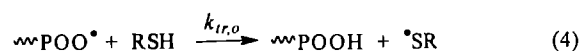


Fig. 1. Photopolymerization of TETGDM at 40°C initiated by 0.001 M BDMB in the presence of 0.001 M MBT or BTDS. Solid line — polymerization in air, dotted line — polymerization in Ar: 1 — no additive, 2 — MBT and 3 — BTDS as additive

obtained is complicated by the fact that both MBT and BTDS absorb the light in the absorption region of BDMB (MBT and BDMB, 10⁻⁴ M in EtOH: λ_{max} within the range of 320–330 nm; BTDS, 10⁻⁴ M in MeOH: λ_{max} ~ 270 nm with a strong shoulder up to ~ 340 nm). Thus, the observed effect results not only from the influence of MBT and BTDS on the polymerization process, but also from screening of the initiator absorption by the additive and from possible additional initiation by photolysis of BTDS. Practically, no influence of the additives investigated on the polymerization in the inert atmosphere was observed, both with 0.01 M (not shown) and with 0.001 M MBT, BTDS and BDMB. In air, each additive retarded the polymerization and decreased the conversion of double bonds. Thus, the effect of chain transfer reaction on the additive molecule [1–6] and slow reinitiation by stabilized RS^{*} radicals [eqns. (1) — (3)] was much more pronounced in air.



The polymerization rate is less reduced by the thiol. The possible explanation is that the thiol reduces the oxygen inhibition in the reaction with peroxy radicals with the formation of thiyl radicals capable of initiating the polymerization:



Reaction (4) reduces the retarding effect of the thiol on the polymerization.

To eliminate the possible effect of photolysis of the additives investigated on the initiation process, another experiment was to initiate polymerization thermally by BPO (Fig. 2).

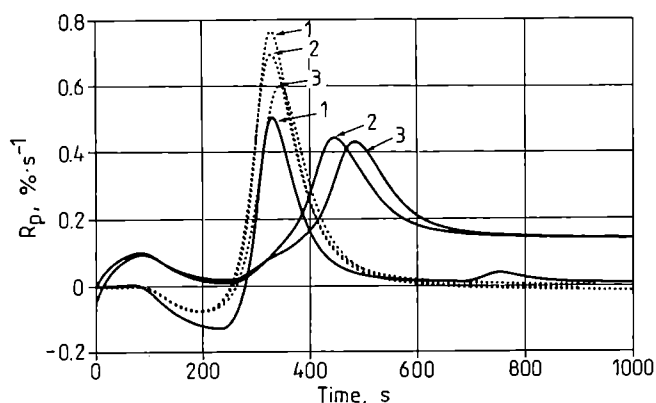


Fig. 2. Polymerization of TETGDM at 80°C initiated thermally by 0.16 M BPO in the presence of 0.01 M MBT or BTDS (for curve symbols, see Fig. 1)

Qualitatively, the result obtained in air was very similar to that observed in the case of UV initiation. In Ar, BTDS reduced the polymerization rate to a degree somewhat higher than did MBT. Thus, considering the effect of MBT and BTDS on the polymerization, we should also take into account: (i) probably different values of chain transfer constants to MBT and BTDS, (ii) the possibility of decomposition of peroxides (both from BPO as well as those formed in the system during illumination in air in the case of photochemical initiation) by thiyl radicals [8].

The kinetic curves of TEGDM photopolymerization initiated by CQ (H-abstraction type initiator) are presented in Fig. 3. In this case, a deeper influence of MBT may be expected, because the excited CQ forms the initiating radicals through hydrogen abstraction (mecha-

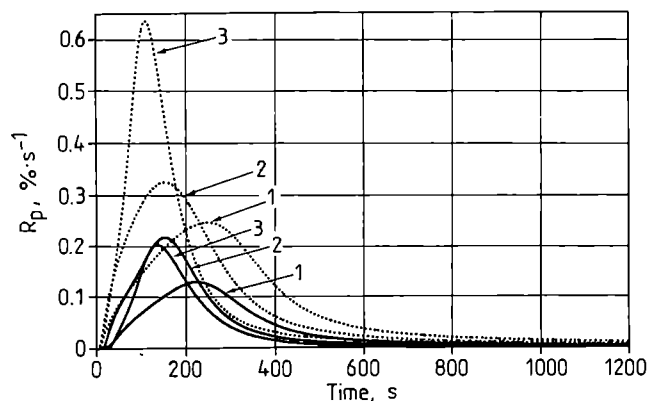
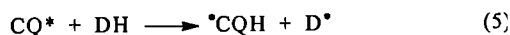


Fig. 3. Photopolymerization of TEGDM at 40°C initiated by 0.12M CQ in the presence of 0.01 M MBT or BTDS (for curve symbols, see Fig. 1)

nism of this reaction may involve electron transfer followed by proton transfer):



where: DH — hydrogen donor molecule (monomer or additive), D* — initiating radical.

Owing to long-wave absorption of CQ ($\lambda_{\text{max}} = 470$ nm), the absorption bands of the initiator and additives do not overlap. The polymerization in the absence of additives is quite efficient, which means that the monomer molecule is able to reduce the excited CQ. Addition of MBT in an almost equimolar amount to CQ eliminates the induction period in air and markedly accelerates the polymerization both in air and in Ar, indicating additional formation of initiating radicals in reaction (5). Thus, MBT is an efficient hydrogen donor for excited CQ.

A surprising result was obtained in the presence of BTDS. In air, BTDS increases the maximum polymerization rate to the value somewhat lower than MBT does, but does not reduce the induction period. On the other hand, in Ar, the accelerating effect of BTDS is very strong and highly exceeds that revealed by MBT. This

may suggest that excited CQ induces cleavage of the -S-S- bond in BTDS.

The present results indicate that the effect of MBT and BTDS on the photopolymerization is a resultant of various processes such as: chain transfer to the additive, slow reinitiation due to stabilization of thiyl radical by the hetero-aromatic moiety, additional initiation due to photolysis of the additive, ability of the additive to reduce type II photoinitiator, generation of thiyl radicals in the reaction of thiols with peroxy radicals, possible decomposition of (hydro)peroxides by thiyl radicals, and screening of initiator absorption by the additive.

Work is in progress.

ACKNOWLEDGMENT

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