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The photopolymerisation of methacrylic acid by colloidal semiconductors

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Summary Methacrylic acid was photopolymerised using CdS and composite, CdS/HgS and CdS/TiO_2, colloidal semiconductor particles as initiators. The previously proposed photoinitiation mechanism involving the photogenerated positive hole in the valence band of the CdS colloid was confirmed by the electron scavenging action of TiO_2. The effect of pH on the course of the polymerisation was investigated and is discussed.

Introduction In a recent paper we described in detail the polymerisation of methyl methacrylate photoinitiated by colloidal cadmium sulphide, a nanocrystalline material [1]. A radical polymerisation mechanism was proposed on the basis of the observed polymerisation kinetics and, especially, thermogravimetric analysis. Specific chain-end structures are formed in the polymer, i.e terminal double bonds adjacent to a tail-to-tail bond.

In this paper we have confirmed the polymerisation mechanism in a more direct manner by using composite semiconductor colloids as polymerisation initiators.

Composite colloids have been synthesised and characterised predominantly in aqueous media [2,3]. Therefore, a water soluble monomer, methacrylic acid, was chosen for these investigations. Besides pure CdS, CdS doped with 1 mol% HgS (HgS on CdS) and CdS/TiO_2 composite colloids were used as polymerisation initiators.

Experimental Methacrylic acid (Aldrich, p.a.) was vacuum distilled before use. The sodium salt of methacrylic acid was synthesised by neutralising methanolic NaOH by a methanolic solution of methacrylic acid [4].

The CdS colloidal solution preparation generally followed a method described by Spanhel et al [3], while HgS was implanted in the surface of CdS by adding the appropriate amount of $Hg(ClO_4)_2$ (1 mol%) to the CdS colloidal solution under stirring [5]. Colloidal TiO_2 was prepared according to ref. 6. The CdS/TiO_2 colloid was obtained by adding $Cd(ClO_4)_2$ to a TiO_2 solution under stirrring and then injecting

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the stoichiometric amount of H_2S. The concentrations of the semiconductor colloidal solutions are given in Table 1.

The polymerisation set-up has been described elsewhere [1]. Methacrylic acid was polymerised by mixing 1 mL of the acid with 3 mL of aqueous CdS or composite colloid. The samples were irradiated at 435.8 nm for up to 60 minutes in 1 cm quartz cells previously bubbled with argon to remove oxygen. The conversion was kept low. The ambient temperature was 27 °C. The incident light intensity, as determined by ferrioxalate actinometry, was 7.0×10^{-6} einsteins/L·s. The pH of the solution was about 2.2.

Sodium methacrylate was polymerised only with CdS. Due to the instability of the colloidal solution, lower concentrations of monomer were used and the solutions were degassed rather than bubbled to remove oxygen. The pH of the solution was about 8.6.

After polymerisation the methacrylic acid samples were freeze-dried, while the sodium methacrylate samples were first neutralised with the required amount of aqueous HCl and then freeze-dried. Corresponding unirradiated, blank runs were also freeze-dried to determine the amount of inorganic substance in the samples. The CdS was removed from the samples by adding 0.1 M aqueous HCl, dialysing the obtained solution and, finally, freeze-drying.

UV Spectra of the samples before and after irradiation were recorded using an OMEGA-10 spectrophotometer (Bruins Instruments, Germany).

The molar mass of the polymers was established by determining the limiting viscosity number, η, of poly(methacrylic acid) (PMA) in methanol at 26°C. The residual colloid stabiliser, polyphosphate, which is insoluble in methanol, was removed by centrifuging. Solutions of polymer samples containing TiO_2 were

Table 1 Concentrations of semiconductor colloidal solutions, molar masses of the resulting polymers and ϕ_{init} , c(acid) = 2.9 mol/L, $I_0 = 7.0 \times 10^{-6}$ einsteins/L·s, irradiation time 60 minutes

Colloid	c(CdS) (mol/L)	c(HgS) (mol/L)	c(TiO_2) (mol/L)	$\overline{M}_n$ (g/mol)	ϕ_{init}
CdS	7.1×10^{-4}			1.32×10^{6}	0.0011
HgS on CdS	7.0×10^{-4}	7.1×10^{-6}		1.41×10^{6}	0.0018
CdS/TiO_2	6.6×10^{-4}		3.30×10^{-3}	7.17×10^{5}	0.0057

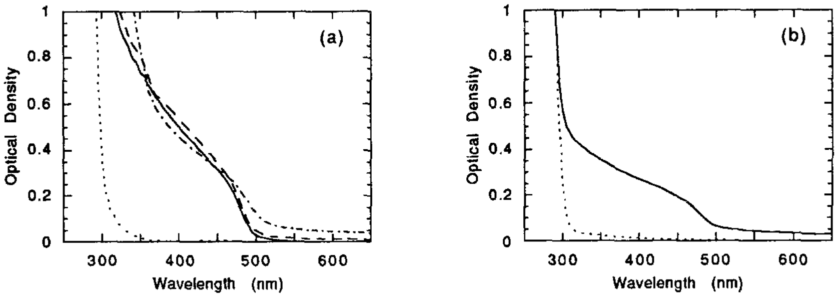

Figure 1 (a) Absorption spectra of colloidal CdS (——), HgS on CdS (- - -) and CdS/TiO_2 (-··-) particles in methacrylic acid aqueous solution (colloidal concentrations specified in Table 1) and of pure methacrylic acid (· · · · ·) and (b) absorption spectra of aqueous solutions of colloidal CdS and Na-methacrylate (——) (c(Na-meth) = 0.85 mol/L, c(CdS) = 2.35×10^{-4} mol/L) and of Na-methacrylate (· · · ·) (c(Na-meth) = 2.27 mol/L), cell pathlength 1 cm

slightly turbid even after centrifuging. The corresponding coefficients of the Kuhn-Mark-Houwink-Sakurada equation, $K = 242 \times 10^{-3}$ mL/g and $a = 0.51$, which yielded the $\overline{M}_n$ of PMA, were taken from the literature[7].

Results and discussion Typical absorption spectra of aqueous methacrylic acid, sodium methacrylate and semiconductor colloidal solutions are shown in Fig. 1. Clearly neither methacrylic acid nor sodium methacrylate absorb any light at 435.8 nm.

The relationships between the polymer yield and the amount of light absorbed by the various colloidal solutions are presented in Fig. 2. The quantum yield of polymerisation of methacrylic acid initiated by CdS ($\phi_{pol} = m_{pol}/(MM_{mon} \cdot h\nu)$ where m_{pol} is the amount of formed polymer, MM_{mon} the molar mass of the monomer and $h\nu$ the amount of absorbed light) was independent of the amount of absorbed light after an initial decrease during the first 20 minutes of irradiation (Fig. 3). Similar behaviour was found in the case of polymerisation initiated by the HgS on CdS colloid. This decrease in ϕ_{pol} might result from PMA chains staying on the the surface of the colloidal particle and hindering monomer access to parts of the particles. The ϕ_{pol} of the CdS/TiO_2 composite colloid was independent of the amount of absorbed light (see Fig. 3). The molar masses $\overline{M}_n$ of the synthesised polymers, as well as the quantum yields of chain initiation, ϕ_{init}, of methacrylic acid samples irradiated for 60 minutes are presented in Table 1 ($\phi_{init} = m_{pol}/(\overline{M}_n \cdot h\nu)$).

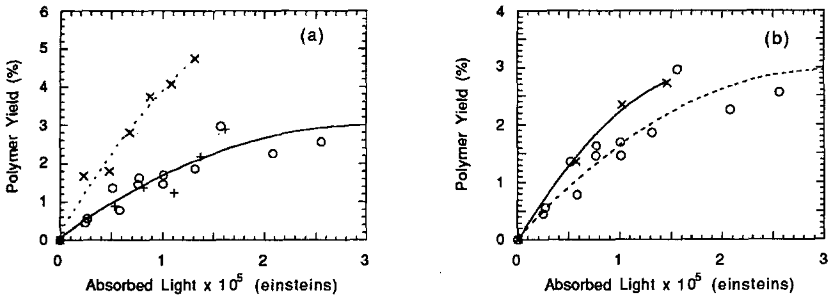

Figure 2 (a) Dependence of the polymer yield on the amount of absorbed light using various semiconductor colloidal initiators: CdS (o), HgS on CdS (+) and CdS/TiO_2 (x); colloidal concentrations specified in Table 1, c(acid) = 2.9 mol/L, $I_0 = 7.0 \times 10^{-6}$ einsteins/L·s, and (b) amount of polymer formed as a function of absorbed light when methacrylic acid (o) (c(acid) = 2.9 mol/L, c(CdS) = 7.1×10^{-4} mol/L, pH = 2.2) and Na-methacrylate (x) (c(Na-meth) = 0.85 mol/L, c(CdS) = 2.35×10^{-4} mol/L, pH = 8.6) are used as monomers, $I_0 = 7.0 \times 10^{-6}$ einsteins/L·s

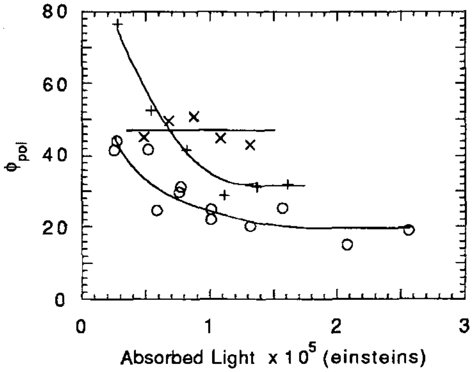

Figure 3 Dependence of ϕ_{pol} of methacrylic acid by various semiconductor colloids on the amount of absorbed light: CdS (o), HgS on CdS (+) and CdS/TiO_2 (x); colloidal concentrations specified in Table 1, c(acid) = 2.9 mol/L, $I_0 = 7.0 \times 10^{-6}$ einsteins/L·s

As proposed previously [1], the positive hole of an excited CdS colloidal particle initiates polymerisation by oxidising the monomer and generating a radical

$$CdS\,(e^-, h^+) + M \longrightarrow CdS\,(e^-)\,H^+ + M\cdot \qquad (1)$$

The efficiency of photopolymerisation can be increased if the positive holes generated in an excited semiconductor colloidal particle can be made more readily available to the monomer.

In the case of HgS on CdS colloids light is absorbed by both the CdS and HgS, although most of the light is absorbed by the CdS due to its much higher concentration. Efficient and fast hole transfer occurs from CdS to HgS when the particles are illuminated, whereas electron transfer takes place much more slowly [5]. The holes on the particle surface where HgS has been implanted in the CdS colloid are susceptible to reaction with the monomer molecules, however, the positive holes in HgS are less oxidising than those in CdS. Therefore, ϕ_{init} does not increase to a large extent in the case of HgS on CdS colloidal particles as compared to CdS even though partial charge carrier separation is achieved in the former case.

When composite CdS/TiO_2 colloids are illuminated, only CdS absorbs light. The behaviour of the composite particles can be understood in terms of electron injection from excited CdS particles into the conduction band of TiO_2 particles [8]. Because of the much more positive potentials of the valence band in TiO_2, the positive hole created by light absorption in the CdS particle remains there. The two partners of the $e^- - h^+$ pair originally generated in a CdS particle find themselves in different parts of the semiconductor particles shortly after excitation, i.e. an efficient charge transfer is achieved.

When CdS/TiO_2 colloidal particles are used as photoinitiators, the positive holes in the CdS islets on the TiO_2 particles are readily available to react with monomer molecules, consequently leading to a higher ϕ_{init} of 0.0057, a five fold increase to the ϕ_{init} of CdS (0.0011).

These results confirm that the proposed photoinitiation of polymerisation by semiconductor colloids, by means of the positive hole, is correct. The TiO_2 serves as an electron scavenger.

It was also necessary to establish whether the acidic hydrogen of methacrylic acid is susceptible to attack by CdS. Therefore, the sodium salt of methacrylic acid was polymerised by CdS. Initially, the results, as shown in Fig. 2b, indicate that the amount of PMA formed as a function of the amount of absorbed light is similar, regardless of whether the acid or salt form of the monomer is employed.

There are not many data available on the rate constants of polymerisation of methacrylic acid at various pH. According to Blauer [9], the overall rate constant of polymerisation at 61.4 °C is $2.0 \times 10^{-4}\ s^{-1}$ at pH 4.1 and 4.2 and then, between pH 4.2 and 5.0, the overall k suddenly decreases by about ten times and stays constant up to pH 12.4. On the basis of the data of Blauer and assuming that all other parameters during the polymerisation are the same, more polymer should be produced when the monomer is polymerised in acidic medium. As this is not the case (see Fig. 2b), it may be concluded that either the acidic hydrogen of methacrylic acid also reacts with the colloidal CdS, thus reducing the efficiency of the photoinitiation of polymerisation, or that, under basic conditions, the methacrylic acid is in its dissociated form which probably enables it to adsorb onto the colloid surface more easily, thus aiding the polymerisation.

Kabanov and coworkers determined the following rate constants for the polymerisation of methacrylic acid at 23 °C: $k_p = 670$ L/mol·s and $k_t = 2.1 \times 10^6$ L/mol·s at pH = 8.0 (the pH being adjusted by NaOH) [10]. Using these rate constants, obtained under conditions which are comparable to the pH 8.6 and 27 °C of our own investigations, the ϕ_{init} of sodium methacrylate by CdS can be approximated from the equation of the rate of polymerisation [1]

$$R_p = k_p\,[M]\left(\frac{\phi_{init}\, I_0\,(1 - e^{-\varepsilon\,[CdS]\,b})}{k_t}\right)^{1/2} \tag{2}$$

where k_p is the rate constant of propagation, L/mol·s, k_t the rate constant of termination, L/mol·s, ε the molar absorptiion coefficient of CdS, L/mol·cm, [CdS] the CdS concentration, mol/L, I_0 the incident light intensity, einsteins/L·s and [M] the monomer concentration, mol/L. (Too little polymer was obtained in these experiments to determine $\overline{M}_n$.)

An approximated ϕ_{init} of about 0.01 for sodium methacrylate initiated by CdS is obtained, which is the same as that for methyl methacrylate polymersation initiated by CdS [1] and considerably higher than that obtained for methacrylic acid photoinitiated by CdS (0.0011). The approximated value of ϕ_{init} of sodium methacrylate initiated by CdS again suggests that either the acidic hydrogen of methacrylic acid is susceptible to reaction, consequently reducing the number of methacrylic monomer radicals initiating polymerisation, or that the methacrylate ion is better adsorbed on the colloidal surface. These two possibilities cannot be distinguished by these experiments.

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References

1. Popović IG, Katsikas L, Müller U, Velickovic JS, Weller H (1994) Makromol. Chem. 195: in press
2. Weller H (1993) Angew. Chem. Int. Ed. Engl. 32: 41

3. Spanhel L, Haase M, Weller H, Henglein A (1987) J. Am. Chem. Soc. 109: 5649
4. McNeill IC, Zulfiqar M (1978) J. Polym. Sci. 16: 3201
5. Hässelbarth A, Eychmüller A, Eichberger R, Giersig M, Mews A, Weller H, (1993) J. Phys. Chem. 97: 5333
6. O'Regan B, Moser J, Anderson MA, Grätzel M (1990) J. Phys. Chem. 94: 8720
7. Brandrup J, Immergut EH (eds) (1989) Polymer Handbook, Third Edition, J. Wiley & Son, New York, pp. VII-10
8. Spanhel L, Weller H, Henglein A (1987) J. Am. Chem. Soc. 109, 6632
9. Blauer K (1960) Trans. Faraday Soc. 56: 606
10. Karaputadse TM, Kurilova AI, Topchiev DA, Kabanov VA (1972) Vysokmol. Soedin. B 14: 323

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