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Comparative Study of the Sonolysis and Radiolysis of Carboxymethylcellulose in Aqueous Solution

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Comparison of the changes in the relative molecular-mass distribution of Na-carboxymethylcellulose on sonolysis, γ-radiolysis and acid hydrolysis in aqueous solutions has shown that sonochemical degradation of Na-carboxymethylcellulose takes place both as a result of mechanical rupture of the macrochains and as a result of the effect of active free radicals from cavitation bubbles, the contributions of the two mechanisms depending on the sonolysis conditions.

The degradation of polymers in aqueous solution under the influence of ultrasound is usually regarded as a mechanochemical process.[1] It is believed that, during the sonolysis of aqueous solutions of high-relative-molecular-mass substances, the macromolecules are ruptured by the action of shock waves during the pulsation and collapse of cavitation bubbles.[2] It has been established experimentally that sonochemical degradation leads to an unusual alteration of the relative molecular-mass distribution (RMMD) of the polymers since longer macromolecules are subjected preferentially to mechanical disruption, chain scission occurring close to the centres of the polymer chains.[2] The relative molecular-mass distribution of a polymer degraded by ultrasound is usually narrower than that for one subjected to statistical degradation with the same number of ruptured bonds. On the other hand, sonochemical reactions in aqueous solutions, involving involatile low-relative-mass substances, are in many respects similar to radiochemical reactions. As a result of secondary reactions after the collapse of the cavitation bubbles, $H^\bullet$ and $OH^\bullet$ radicals pass into the solution on exposure to ultrasound. $HO_2^\bullet$ and solvated electrons are also formed in the presence of oxygen. The active species formed subsequently enter into various reactions with substances dissolved in the water.[4] Evidently, during sonolytic polymer degradation active radicals originating from cavitation bubbles interact with the macromolecules, producing a radiation-type degradation, which is statistical in character, unlike mechanochemical degradation. It is of interest to investigate the conditions under which a particular sonolysis mechanism occurs preferentially for a specific polymer. The nature of the changes in the relative molecular-mass distribution on acid hydrolysis, sonolysis and γ-radiolysis of Na-carboxymethylcellulose was, therefore, compared under various conditions using the approach already described.[5]

The sodium salt of carboxymethylcellulose (Na-CMC) (Serva) with a degree of substitution of 0.7 was used in the present study. Aqueous Na-CMC solutions (5, 10 and 20 g dm^{-3}) were irradiated with ^{60}Co γ-rays in air and nitrogen at a dose rate of 5.4 kGy h^{-1}.†

Acid hydrolysis of Na-CMC was carried out with 0.09 mol dm^{-3} HCl at a Na-CMC concentration of 18 g dm^{-3} at 100°C. The concentration of reducing groups in the hydrolysed reaction mixtures was measured by the Somogi–Nelson method.[6] The number-average degree of polymerisation $\bar{X}_n$ was calculated from the formula $\bar{X}_n = c_{CMC}/[RG]\bar{M}_{r,m}$, where c_{CMC} is the concentration of Na-CMC (g dm^{-3}), [RG] the concentration of the reducing groups (mol dm^{-3}), and $\bar{M}_{r,m}$ the average relative molecular mass of the monomeric unit, which can be assumed to be 217 g mol^{-1} for a degree of substitution of 0.7.

Sonolysis of solutions of Na-CMC was carried out at 30°C in a special cell ensuring the passage of the ultrasound beam through the solution without the formation of standing waves, resulting in constant sonolysis parameters. The ultrasonic frequency was 724 kHz and the acoustic power output was 30 W. The volume of liquid in the cell was 40 ml.

The viscosities of the Na-CMC solutions were measured using an Ubbelohde viscometer at 25°C in 0.05 mol dm^{-3} ammonia–acetate buffer at pH 4.5 with added 0.1 mol dm^{-3} NaCl. The intrinsic viscosity [η] was determined from eqn. (1), extrapolating the concentration dependence of $(\eta_r - 1)/c_{CMC}$ to $c_{CMC} = 0$, where η_r is the relative viscosity.

$$[\eta] = \lim_{c \to 0} (\eta_r - 1)/c_{CMC} \qquad (1)$$

The radiochemical yields of the degradation of Na-CMC were calculated by means of relation (2), where n is the mass

$$1/\bar{X}_n - 1/\bar{X}_{n0} = (\bar{M}_{r,m}/100 N_A \mathrm{n})\bar{G}_{degr} D \times 6.24 \times 10^{15} \qquad (2)$$

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† Gy = J kg^{-1}.

Table 1 Degradation of Na-CMC in aqueous solution by acid hydrolysis, γ-radiolysis and sonolysis

Sample	Degradation agent,[a] exposure/min	Saturating gas	Concentration /g dm^{-3}	10 $[\eta]$/dm^3 g^{-1}	$\bar{X}_n$[b]	$10^2\,\bar{G}_{degr}$/eV
1	Original CMC	—	—	3.5	350	—
2	H^+, 10	—	18	1.68	168[b]	—
3	H^+, 21	—	18	1.25	125[b]	—
4	H^+, 24	—	18	1.10	110[b]	—
5	H^+, 35	—	18	0.40	45[b]	—
6	γ, 30	N_2	5	0.42	42[c]	1.9
7	γ, 30	O_2	5	0.42	42[c]	1.9
8	γ, 15	N_2	10	1.30	130[c]	1.7
9	γ, 30	N_2	10	0.89	89[c]	1.5
10	γ, 15	O_2	10	1.08	108[c]	2.3
11	γ, 30	O_2	10	0.70	70[c]	2.0
12	γ, 30	N_2	20	1.62	162[c]	1.2
13	γ, 30	O_2	20	1.25	125[c]	1.8
14	US, 180	N_2	5	1.11	—	—
15	US, 180	O_2	5	1.12	112	—
16	US, 180	N_2	10	1.26	—	—
17	US, 180	O_2	10	1.57	—	—

[a] H^+ = acid hydrolysis, γ = γ-radiolysis, US = ultrasound. [b] Determined from the reducing groups. [c] Calculated from eqn. (3).

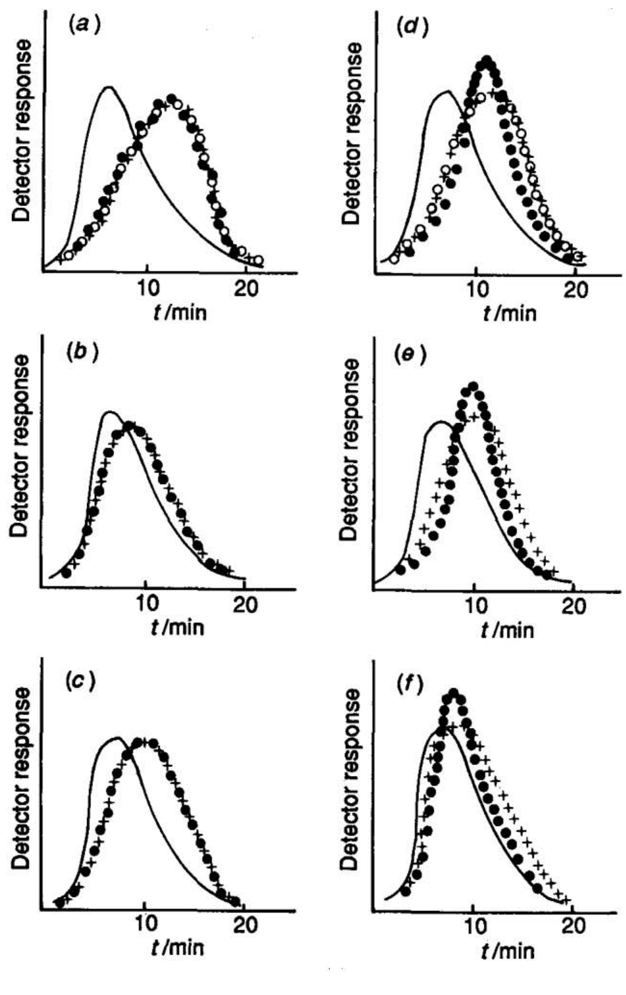

Fig. 1 Gel-chromatograms of an initial aqueous solution of Na-CMC (continuous line) and after degradation by acid hydrolysis, γ-radiolysis and sonolysis. (*a*) Samples 5 (+), 6 (○) and 7 (●); (*b*) 2 (+) and 12 (●); (*c*) 3 (+) and 13 (●); (*d*) 4 (+), 14 (●) and 15 (○); (*e*) 3 (+) and 16 (●); (*f*) 2 (+) and 17 (●). See Table 1 for degradation conditions.

fraction of Na-CMC in solution, $\bar{X}_n$ and $\bar{X}_{n0}$ are the number-average degrees of polymerisation of Na-CMC after γ-irradiation and of the initial Na-CMC respectively, N_A is the Avogadro number, $\bar{G}_{degr}$ is the radiochemical yield (10^{-2} eV^{-1}) and D is the absorbed dose (Gy).†

Gel chromatography of the Na-CMC solutions was performed using a Bio-Rad HPLC system under the following conditions: two series-connected 7.5 × 600 mm TSK-50XL and TSK-30XL columns, temperature 20 °C, eluent 0.05 mol dm^{-3} ammonia–acetate buffer at pH 4.5 with added 0.05 mol dm^{-3} NaCl, rate of elution 1.2 ml min^{-1}, pressure at the column inlet 6 MPa, refractometric detector, volume of injected sample 100 μl, Na-CMC concentration in the sample 4 g dm^{-3}.

Experimental data for the acid hydrolysis, γ-radiolysis and sonolysis of aqueous Na-CMC solutions under various conditions are presented in Table 1, while Fig. 1 shows the superposition of the gel-chromatograms of various pairs of samples. It can be seen from Figs. 1(*a*)–(*c*) that gel-chromatograms of the hydrolysed reaction mixtures and the irradiated samples having the same values of $[\eta]$ are identical. Consequently, γ-radiolysis of Na-CMC in aqueous solution takes place in the same way as acid hydrolysis, *i.e.* statistically, like the radiolysis of solid Na-CMC.[5] This allows us to use relation (3), obtained from the acid hydrolysis data to determine $\bar{X}_n$ and

$$[\eta] = 0.001\bar{X}_n \text{ dm}^3\text{ g}^{-1} \qquad (3)$$

$\bar{G}_{degr}$ of the irradiated samples from their intrinsic viscosities. The relation presented above [eqn. (3)] agrees well with that obtained previously.[5] The calculated values of $\bar{X}_n$ and $\bar{G}_{degr}$ are listed in Table 1. At low Na-CMC concentrations in solution (5 g dm^{-3}), $\bar{G}_{degr}$ is independent of the saturating atmosphere (air or N_2). For samples saturated with N_2, $\bar{G}_{degr}$ decreases significantly with increase in the Na-CMC concentration. This concentration effect can be explained in terms of competition between a macroradical decomposition reaction and a radical centre transfer reaction, as a result of which degradable macroradicals are converted into non-degradable ones. The presence of O_2 in the irradiated polymer solutions eliminates the dependence of $\bar{G}_{degr}$ on the Na-CMC concentration. As for aqueous solutions of other degradable polymers, *e.g.* poly(ethylene oxide), the observed effect of O_2 can be explained by the reaction of oxygen with the macroradicals to form peroxymacroradicals, which subsequently decompose.[7]

Let us consider the results of the sonolysis experiments. Superposition of the gel-chromatograms of the hydrolysed reaction mixtures and UV-irradiated Na-CMC solutions shows that statistical degradation is observed only in a dilute solution containing only O_2 [Fig. 1(*d*), sample 15, Table 1]. Examination of the corresponding superimposed chromatograms [Figs. 1(*e*) and (*f*)] shows that in the remaining cases degradation leads to a narrower relative molecular-mass distribution than does the statistical degradation. Thus, on sonolysis of Na-CMC solutions there is a possibility of both preferential mechanical rupture of the longest polymer chains and statistical rupture caused by active species derived from the water. The contributions of these two mechanisms vary depending on the sonolysis conditions. Bearing in mind that similar values of $[\eta]$ (samples 14 and 16 in Table 1) were obtained for solutions subjected to ultrasound under an argon atmosphere and containing Na-CMC at concentrations of 5 and 10 g dm^{-3}, one may conclude that an increase in the Na-CMC concentration on sonolysis accelerates the degradation by accelerating the mechanochemical rupture of the polymer chains. Indeed, it follows from the radiolysis data that the degradation occurring under the influence of active species from water is suppressed with increase in the concentration of the polymer in the initial solution. This conclusion agrees with the generally-held view on the mechanism of mechanochemical degradation, that the rate of degradation of a polymer should increase with increase in its concentration in solution because this entails an increase in the number of macromolecules entering regions of high velocity gradients in the shock waves generated on cavitation.

It is of interest to estimate the sonochemical yield $\bar{G}_{s,degr}$ of the degradation of CMC. This can be done for sample 15, since its relative molecular-mass distribution is nearly statistical, using a formula similar to eqn. (2) [eqn. (4)], where E is the

$$1/\bar{X}_n - 1/\bar{X}_{n0} = (\bar{M}_{r,m}/100 N_A\, n)\bar{G}_{s,degr} E \times 6.24 \times 10^{15} \quad (4)$$

absorbed acoustic energy per g of solution (Gy). Assuming that the entire energy of the ultrasound radiation is absorbed by the sample (this was confirmed calorimetrically), one can obtain $E = 1.082 \times 10^7$ Gy from the acoustic power, the weight of the liquid in the cell and the sonolysis time and then $\bar{G}_{s,degr}$ 1.25×10^{-4} bonds/100 eV results from eqn. (4). Comparison of the result with the radiochemical yield implies that the energy efficiency of the chemical action of ultrasound in the given system is lower by four orders of magnitude than that of ionising radiation.

References

1 N. K. Baramboym, *Mekhanokhimiya polimerov* (Mechanochemistry of polymers), Khimiya, Moscow, 1978, pp. 264–73 (in Russian).

2 M. Cutierrez and A. Henglein, *J. Phys. Chem.*, 1988, **92**, 2978.

3 G. J. Price, *Adv. Sonochem.*, 1990, **1**, 254.

4 M. A. Margulis, *Osnovy zvukokhimii* (Fundamentals of sonochemistry), Vysshaya Shkola, Moscow, 1984, p. 114 (in Russian).

5 V. U. Ufimtsev, A. S. Glukhikh, G. V. Kovalev, A. P. Sinitsyn and L. T. Bugaenko, *Vestn. Mosk. Univ., Ser 2: Khim.*, 1989, 30 (in Russian).

6 A. A. Klyosov, M. L. Rabinovich, A. P. Sinitsyn, I. V. Churilova and S. U. Grigorash, *Bioorg. Khim.*, 1980, **6**, 1225 [*Sov. J. Bioorg. Chem. (Engl. Transl.)*, 1980, **6**, 662].

7 A. K. Pikaev, *Sovremennaya radiatsionnaya khimiya. Tverdoe telo i polimery* (Modern radiochemistry. Solid state and polymers), Nauka, Moscow, 1987, p. 204 (in Russian).

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