Microgels—Functional Globular Macromolecules

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ABSTRACT: Reactive microgels are crosslinked macromolecules of globular shape. They may be prepared by polymerization of multifunctional monomers in emulsion or solution. Microgels are soluble in water or organic solvents. Their molecular mass is usually much higher than that of linear macromolecules of comparable diameters. By emulsion copolymerization (ECP) of unsaturated polyesters (UP) and styrene (S) microgels may serve as self-emulsifying component in ECP. Results on influence of molecular mass of UP and UP/S ratio on microgel yield, on the relation between structure and viscosity of microgel solution and on the ageing mechanism in dry state are reported.
    KEY WORDS   Microgels / Crosslinked Globular Macromolecules / Emulsion Copolymerization / Unsaturated Polyester Resins / Colloids / Ageing /

Molecular structures of polymers are linear, branched or crosslinked. In the first two cases, the polymers consist of independent macromolecules, each of which possesses the structural characteristics of the polymer.

Crosslinked polymers have been sometimes described as super macromolecules, whose dimensions are identical with those of the reaction batch or with the object, which is composed of them. However this definition is unsatisfactory because it blurs the differences between a molecule and a solid, and because properties characteristic for a macromolecule are missing.

It has been shown, that real crosslinked macromolecules can be prepared by emulsion or solution polymerization of tetra- or multifunctional monomers.[1] In solution polymerization crosslinking of the whole reaction batch may be largely suppressed by using high-functional monomers only or in large excess.[2] Such crosslinked macromolecules may be considered as a new class of polymers and have been also designated microgels. Microgels are independent, globular macromolecules with a crosslinked structure. Their dimensions are comparable with coil diameters of linear or branched macromol-

ecules. Microgels may be dissolved in suitable solvents. Depending on the molecular mass and structure the appearance of these solutions may vary from clear to bluish, yellowish or faintly turbid, corresponding to the size of particles in colloidal solutions. Due to the crosslinked structure microgel solutions have much lower viscosity than solutions of linear or branched macromolecules of comparable molecular mass.

Microgels have been also prepared by emulsion copolymerization of unsaturated polyesters (UP) and styrene (S).[3] Depending on the ratio unsaturated polyester/styrene (UP/S by wt) and the monomer concentration crosslinked coagulate, microgels or a macrogel may be obtained.[4,5] In the following, results on the molecular structure, their relation to viscosity and the mechanism of ageing of UP/S-microgels are reported.

INFLUENCE OF THE MOLECULAR MASS OF THE UP AND THE UP/S-RATIO ON THE YIELD OF MICROGELS

As has been described earlier[4,5] a maximum yield

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Table I. Yield of microgels and M_n of UP
(ECP, 3 h, 70°C; serum ratio, 1 : 30;
initiator AIBN. UP, MAA + HD;
FA/MA = 1/2; terminal
groups, –COOH.)

M_n	Yield, % by wt	
	Coagulum	Microgel
1170	—	10
1470	—	25
1750	—	92
2140	—	96
2600[a]	90	—
3850[a]	90	—

[a] UP in alkaline water: turbid, instable suspension.

Table II. UP/S ratio and structure of the
copolymer (ECP, see Table I. UP, M_n =
2140; acid no. 0.94 meq g^{-1};
hydroxyl no. $\approx 10^{-4}$ meq g^{-1}.)

UP/S by wt	Main product of ECP	Solution in dioxane
30 : 70	Coagulum	Emulsion
40 : 60	Microgel	Bluish transp. soln.
50 : 50	Microgel	Bluish transp. soln.
60 : 40	Macrogel	Emulsion
70 : 30	Macrogel	Emulsion

Table III. Influence of degree of neutralization
of UP on yield and composition of microgel
(Mg) and coagulum
(ECP, 24 h; 70°C; UP/S = 40/60; serum ratio
1 : 5; initiator, AIBN 10^{-2} mol l^{-1};
emulsifier, Triton 405® 3 g l^{-1}.)

Degree of neutralization	Yield/wt%			UP-content/ wt%	
%	Mg	Coag	Total	Mg	Coag.
0	15.0	63.3	78.3	21.4	47.9
15	15.8	64.1	79.9	25.6	47.1
30	17.0	63.8	80.8	30.9	46.9
50	19.2	63.6	82.8	36.1	46.3
65	20.9	63.3	84.2	41.8	45.6
80	21.8	64.1	85.9	45.2	44.2
100	23.5	64.5	88.0	52.4	43.9

of microgels in emulsion copolymerization with UP as comonomer is only possible with UP-fractions of medium molecular weight. In case of an UP from maleic anhydride (MA) and hexanediol-1,6 (HD), with UP-fractions of low molecular weight fractions only low yields of microgels were obtained (Table I). UP-fraction of a molecular mass between about 1700 and 2200 have optimal self-emulsifying properties. Another limitation is the UP/S-ratio. As shown in Table II with a low fraction of UP mostly coagulum is formed whereas at high fractions of UP the main product is a macrogel.

SELF-EMULSIFICATION OF UP-MOLECULES IN EMULSION COPOLYMERIZATION WITH STYRENE AS COMONOMER

An UP from MA and HD (FA/MA = 1 : 2) with carboxyl endgroups in the acid form dissolves re-adily in styrene. For copolymerization in emulsion poly(oxyethylene)-octyl phenyl ether was used as an external emulsifier. At the beginning the UP/S-ratio of both monomer droplets and micells corresponds to the initial batch ratio. Copolymerization has been initiated by oil-soluble AIBN in droplets as well as in micells. As UP-molecules are very little soluble in water, predominantly styrene diffuses to micells resp. growing microgel particles. Therefore, besides a large amount of polymerized and crosslinked monomer droplets, which form an insoluble coagulum, a small amount of microgels is formed with an UP/S-ratio which ißcreases with the degree of neutralization (Table III).

With increase of pH, acid endgroups are converted to the salt form and more UP-molecules collect at the droplet surface and also diffuse into the aqueous phase to form more and smaller micells. Correspondingly the yield of microgels and their UP-fraction increases. In presence of the nonionic emulsifier coagulum is formed. This can be avoided by using a fully neutralized UP as self-emulsifying comonomer without an external emulsifier. In this case no coagulum is formed and microgels are obtained in high yields (Table IV). Neutralization of the UP is complete between pH 7.1 and 7.7. Below pH 7 the only product is a macrogel (Figure 1).

On complete neutralization and absence of an external emulsifier UP-molecules do not dissolve in the monomer droplets but are present at their

Table IV. pH in self-emulsifying ECP of UP ($M_n=2100$), carboxyl group content and UP composition of microgels (Mg)

pH	UP/S batch ratio wt	Mg-yield wt%	Acid no. of Mg mmol g^{-1}	Fraction of –COOH at Mg-surface %	UP-content of Mg wt%
6.0	40/60	—	—	—	—
7.1	40/60	56	0.147	39	35.1
7.7	40/60	84	0.210	56	38.9
8.3	40/60	93	0.188	50	39.8
9.0	40/60	87	0.191	51	39.1
9.9	40/60	63	0.185	50	38.0
10.0	40/60	75	0.210	52	38.2
7.9[a]	40/60	85	0.230	62	39.8
8.0[a]	40/60	96	0.221	54	39.6
7.4	60/40	75	0.366	60	59.1
10.0	60/40	68	0.385	63	59.0

[a] Based on UP-fraction of Mg, determined by oxygen content.

MONOMER DROPLETS

PH > CA.8   PH < CA.7

POLYMERISATION (AIBN)

MICROGEL ONLY
(CA.50% OF CARBOXYLGROUPS
LOCATED AT PARTICLE SURFACE)

MACROGEL ONLY
(CROSSLINKED DROPLETS)

●—● UP-MOLECULE, CARBOXYL ENDGROUPS, NON-DISSOCIATED
●—O UP-MOLECULE, CARBOXYL ENDGROUPS, PARTLY DISSOCIATED
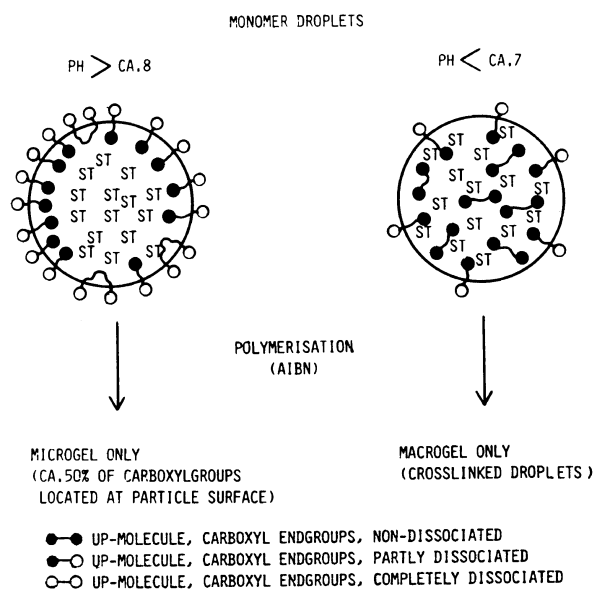O—O UP-MOLECULE, CARBOXYL ENDGROUPS, COMPLETELY DISSOCIATED

Figure 1. Influence of pH on formation of microgels resp. coagulum in self-emulsifying copolymerization of UP-styrene (60/40). UP (hexanediol-MA), $M_n=2140$, $\overline{DB}=11$.

surface. As the total surface of the UP-micelles is much larger than that of the droplets, most of the UP-molecules are already on the micell surfaces and the droplets mainly supply growing microgel particles with styrene. On complete neutralization about 50% of the carboxyl groups stay at microgel surface and the composition of the microgels almost corresponds to the original UP/S-ratio (Table IV). With increase of the UP/S batch ratio the number of carboxyl groups at microgel
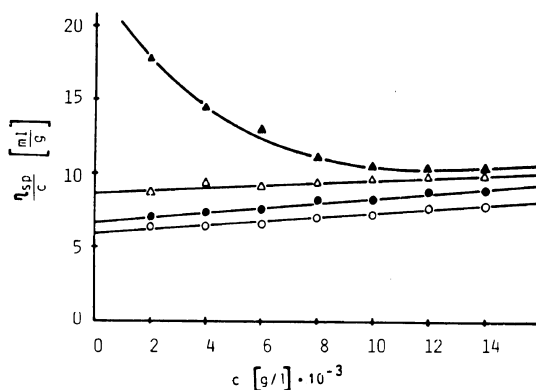
Figure 2. Dependence of η_{sp}/c of dilute MG-solutions on solvent. $K_2S_2O_8$-microgel in dioxane ($\triangle$) and in MEK ($\blacktriangle$) AIBN-microgel in dioxane ($\bigcirc$) and in MEK ($\bullet$).

surfaces increases as well as the UP-content.

VISCOSITY AND MOLECULAR STRUCTURE OF UP/S-MICROGELS

Microgels, which are prepared from UP-resins by emulsion copolymerization, are crosslinked macromolecules, which, contrary to crosslinked polymers, dissolve in suitable organic solvents. Therefore viscosity measurements are possible, and such data may be related to structural parameters like crosslink density.

As shown in Figure 2 the reduced viscosity of microgels from $K_2S_2O_8$-initiated emulsion copolymerization of UP-S increased towards low microgel concentrations. As due to the crosslinked structure an electrostatic repulsion of dissociated acid groups and corresponding coil expansion is not probable, an electro-viscous effect[6,7] is probably responsible for this increase of η_{red} toward $c = 0$. In a solvent with a low dielectric constant, like dioxane, the relationship bweeen η_{sp}/c and c was linear. Microgels from AIBN-initiated emulsion copolymerization of UP-S did not show a viscosity anomality, neither in dioxane nor in MEK. Therefore the polyelectrolyte effect is probably caused by strongly acid sulfate endgroups, which have been introduced by sulfate radical anions. Carboxyl acid end-groups obviously are scarcely dissociated, even in more polar solvents.

To avoid viscosity anomalies microgels prepared by AIBN were used for viscosity measurements.
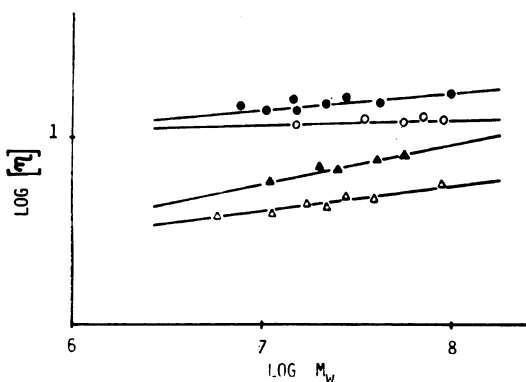

Figure 3. Influence of UP/S ratio in ECP on the $[\eta] - M_w$ relationship of the respective microgels. UP/S = 40/60. $\blacktriangle$, A = 0.21; UP/S = 60/40, $\triangle$, A = 0.313; UP/S = 25/75, $\bullet$, A = 0.09; UP/S = 40/60, $\bigcirc$, A = 0.03. UP is partially terminated by phthalic acid units for $\bullet$ and $\bigcirc$.

As microgels are crosslinked macromolecules of globular shape, they swell very little or not at all in organic solvents. Therefore their solutions should behave according to Einstein's law of viscosity. As may been seen from Figure 3 $[\eta]$ scarcely depends on molecular mass. For given UP/S-ratios coil density and also crosslink density does not depend significantly on molecular mass.

Increasing the UP-fraction, however, increases crosslink density and accordingly the more compact microgels of same molecular mass have lower intrinsic viscosities (Figure 3). If an UP with a higher functionality is used, the microgels have a higher
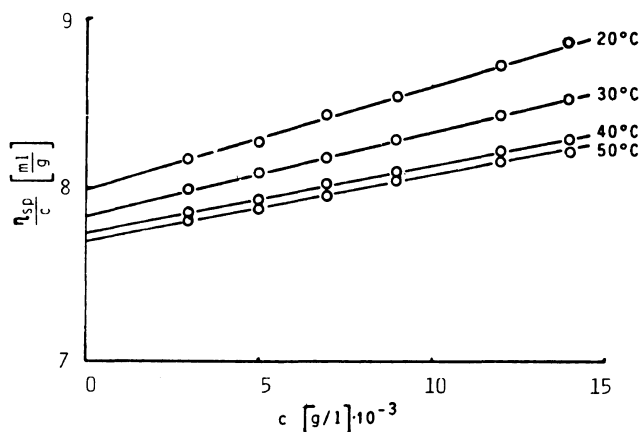
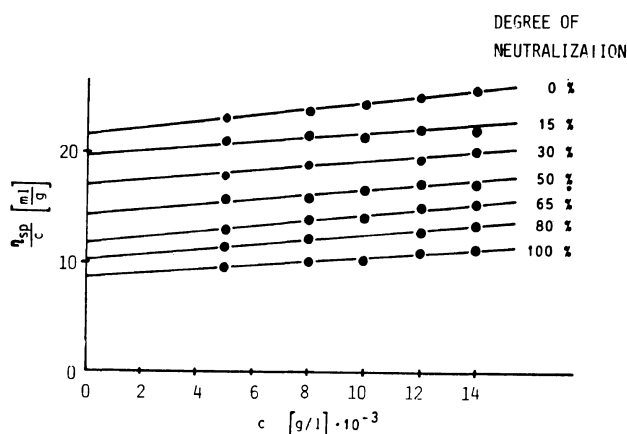**Figure 4.** Dependence of η_{sp}/c on [MG] in dioxane.

Figure 5. Influence of degree of neutralization in EP of UP/S on η_{sp}/c *vs. c* in dioxane.

crosslink density and also lower reduced viscosities.

The Huggins constants of UP-microgels are small ($k_H = 0.02 - 0.2$), so are the exponents of the relation between intrinsic viscosity, [η] and molecular mass,* M_w ($a = 0.03 - 0.21$). This agrees with a compact structure and little swellability of these microgels. The equivalent density is also high ($\rho_{eq} = 0.316$ g cm^{-1}) and thermal effects on reduced viscosity are very small (Figure 4). [η] and slope of η_{sp}/c *vs. c*-isotherms decrease only a little between 20 and 50°C.

It has been shown earlier[8] that terminal unsaturated maleic or fumaric acid units do not participate in copolymerization due to the electronic interaction of the carboxylate anion end group with the double bond. It may be expected therefore that on ECP the degree of dissociation of acid end groups influences the microgel structure. Therefore the degree of neutralization was varied up to the acid-base equivalence. As shown in Figure 5 it decreases on approaching the acid-base equivalence. Simultaneously the UP-content of the microgels increases (Table III) which means an increase in crosslink density. On the contrary rather an increase of [η] would have to be expected due to pendant chains with non-reacted terminal dicarbonic acid units. It may be concluded therefore, that the decrease of [η] is due to increasing crosslink density. If the UP-fraction of microgels and thereby also their crosslink density is kep constant, neither [η]

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* The molar mass of the microgel, M_w, was determined by laser light scattering measurements (Chromatise®).

Table V. Effect of degree of neutralization on $[\eta]$ and $k_H [\eta]^2$ at constant UP-content of the Mg. Emulsifier Triton X 405®

Degree of neutral. on EP %	UP-content of Mg wt%	$[\eta]$ ml g^{-1}	$k_H [\eta]^2$
0	38.1	13.5	0.20
30	37.6	14.7	0.22
50	36.1	14.3	0.21
75	36.8	13.8	0.19
100	38.1	15.1	0.22

Table VI. Effect of pH on $[\eta]$ and $k_H [\eta]^2$ in self-emulsifying ECP of UP-S UP/S = 40/60

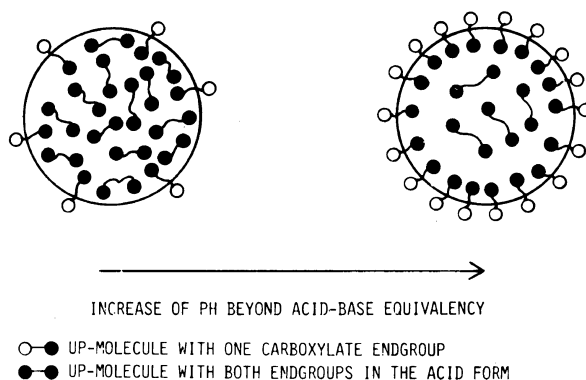| pH	$[\eta]$ ml g^{-1}	$k_H [\eta]^2$
7.1	5.91	0.05
7.7	7.00	0.04
8.3	7.81	0.06
9.0	8.44	0.10
9.9	11.43	0.13
10.0	10.70	0.12
7.9	5.62	0.03
7.4	4.58	0.03[a]
10.0	11.04	0.15[a]

[a] UP/S = 60/40.
[a] Buffered by NaHCO$_3$.

Table VII. Chain length and $[\eta]$ in copolymer and polyester chains of Mg; $M_w = (18—21) \times 10^6$

UP/S wt%	Chain length (basic units)		$[\eta]$ ml g^{-1}
	Copolymer	Polyester	
30/70	18	23	6.64
40/60	13	25	5.89
50/50	11	33	4.87
60/40	8	40	4.58
70/30	8	—[a]	6.34
23/77	30	12	16.04
26/74	27	12	14.93
34/66	21	12	11.75
44/56	16	12	11.03

[a] Not accessible to calculation because double bonds are not uniformly distributed on the UP-chains.

nor the slope of the Huggins equation varied significantly with the degree of neutralization (Table V).

In self-emulsifying ECP of UP-S mixtures more than 80% of the carboxylic acid end groups must be neutralized in order to avoid formation of coagulum. If the pH-value is increased beyond the acid-base equivalent, the UP-content of the microgels remains constant (Table IV), but $[\eta]$ and $k_H [\eta]^2$ increases (Table VI). A rise of pH means increasing the amount of carboxylate groups, which prevent polymerization of the adjacent double bond of the partially esterified terminal maleic or fumaric acid units. It may be also expected that UP-molecules increasingly accumulate at the surface of the grow-

INCREASE OF PH BEYOND ACID-BASE EQUIVALENCY

○—● UP-MOLECULE WITH ONE CARBOXYLATE ENDGROUP
●—● UP-MOLECULE WITH BOTH ENDGROUPS IN THE ACID FORM

Figure 6. Schematical representation of the influence of increasing pH on the microgel structure (styrene molecules have been omitted!)

ing particle, thus depleting its interior from cross-linking polyester molecules (Figure 6). Both effects decrease crosslink density and explain why $[\eta]$ and $k_H\,[\eta]^2$ increase with the pH-value.

If the UP-fraction in the copolymerization batch is increased the crosslink density along the co-polymer network chain and, accordingly also $[\eta]$ decreases (Table VII). A concurrent decrease of crosslink density along the polyester chain ob-viously does not much effect $[\eta]$.

Correspondingly, an increase of crosslink density along the copolymer chains at constant crosslink density along the polyester chains reduces $[\eta]$. It may be concluded therefore, that the crosslink density along the copolymer chains dominates in determining the structural density of microgel par-ticles and thereby $[\eta]$.

AGEING MECHANISM OF UP/S MICROGELS

In solid state reactive microgels, obtained by emulsion polymerization of divinylbenzene or ethyl-englycol dimethacrylate, become rapidly insoluble, despite of freeze-drying and storage under nitrogen at $-40°C$.[9] Likewise UP-S microgels gradually be-come insoluble, whereas solutions in dioxane re-main stable for a long time and no precipitate is formed. Even in unsaturated polyester from MA and HD on long storage insoluble fractions have been observed. Acid and hydroxyl number of the soluble fraction remains unchanged but an increase in molecular weight has taken place.

Insolubility as a result of an ageing process is a common phenomena of microgels. For the ageing process of UP-S microgels it could be shown that insolubility is caused by radical crosslinking of microgel particles. It is reasonable to assume that residual fumaric or maleic acid terminal units of the UP are responsible for crosslinking. However no significant change of unsaturation was found by IR spectroscopy. On the other hand, for the formation of irreversible agglomerates from reactive microgels with high surface functionality, only very few chemical bonds are necessary to enlarge particle size beyond the border of solubility. Residual unsatu-ration of microgels from varying UP/S-batch ratios is shown in Table VIII. After bromination still a substantial amount of unsaturation is left, probably due to inaccessibility of the double bonds.

The rate of ageing has been measured by the increase of the insoluble fraction of microgels at

Table VIII. Residual unsaturation of Mg and initial UP/S ratios

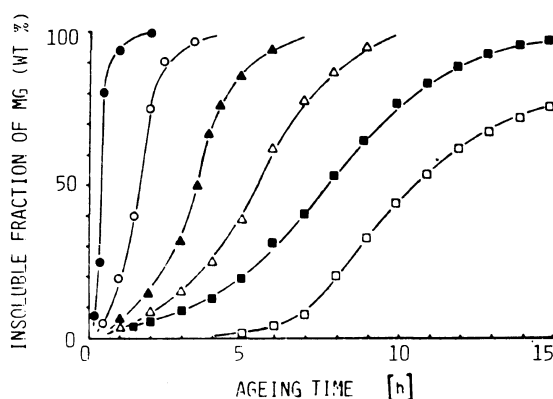| UP/S by wt	Resid. unsat. based on UP-fraction in Mg %	Resid. unsat. after Br-addition
30/70	42.8	30.6
40/60	45.7	36.4
50/50	56.3	43.8
60/40	59.8	48.6
70/30	70.2	52.8

Figure 7. Insoluble MG-fraction on ageing. N_2: 70°C (●), 60°C (▲), 50°C (■); O_2: 70°C (○), 60°C (△), 50°C (□).

Table IX. Soluble fraction of Mg after ageing with varying amounts of hydroquinone

mg hydro-quinone/mol COOH	Soluble fraction of Mg after ageing wt%				
	1 h	2 h	3 h	5 h	10 h
0	6.6	—	—	—	—
1	96.0	42	8	—	—
5	100.0	89	73	21	—
10	100.0	100	100	86	18

Table X. $[\eta]$ of soluble Mg-fractions after ageing at 50°C under O_2

Ageing time	$[\eta]$	Slope	$M_w \times 10^{-6}$
h	ml g^{-1}		
0	7.29	0.014	33.6
1	7.36	0.040	34.7
2	7.58	0.041	40.1
3	7.59	0.059	40.3
4	8.03	0.051	52.6
5	8.33	0.046	62.8
6	8.79	0.052	80.9
7	8.87	0.054	84.3
8	8.95	0.048	88.0
9	9.02	0.049	91.6
10	8.97	0.047	89.3

Table XI. $[\eta]$, ageing time and ultrasonic treatment of agglomerated microgels (ageing conditions: 70°C, N_2)

Ageing time	Ultrasonic treatment	Soluble fraction	$[\eta]$	$k_H [\eta]^2$
h	h	wt%	ml g^{-1}	
0	—	—	8.06	0.045
	24	—	8.12	0.042
1	8	71	8.63	0.071
	12	100	8.42	0.063
	24	100	8.30	0.061
3	12	12	8.64	0.069
	24	33	8.56	0.062
10	24	—	—	—

Table XII. $[\eta]$ of soluble fraction of aged microgels on storage at $-30°C$

t/month	$[\eta]$/ml g^{-1}	
	O_2	N_2
0	7.84	7.84
1	7.95	8.06
2	7.94	8.09
3	7.93	7.97
4	7.98	8.08
7	7.96	8.04
10	7.95	8.05

different temperatures when stored under nitrogen resp. oxygen. As shown in Figure 7 under oxygen insolubility develops slower than under nitrogen. Oxygen as a biradical retards interparticle crosslinking of microgels in the same way as radical polymerization. The accelerating effect of temperature increase also agrees with the radical nature of the crosslinking reaction. Accordingly addition of hydroquinone as a radical inhibitor suppresses insolubility by ageing (Table IX).

It may be concluded therefore, that ageing of UP-S-microgels is the result of topochemical radical reactions between reactive surface groups of primary microgel particles. The increase of particle size is reflected in an increase of $[\eta]$ and of the molecular weight (Table X). M_w has been calculated by the Mark-Houwink-Sakurada equation with constant $K = 0.192$ and exponent $a = 0.21$.

Up to about 6 h ageing, $[\eta]$ and M_w increases, due

to formation of soluble microgel agglomerates. Later on both values remain constant but the fraction of insoluble microgel agglomerates increases strongly (Figure 7). As for the formation of insoluble microgel agglomerates only a few interparticle bonds are necessary it is possible to redissolve microgel agglomerates to some extent by shearing forces. With increasing length of ultrasonic treatment the soluble fraction of equally aged microgel agglomerates increases (Table XI). Ultrasonic treatment of unaged microgels does not affect $[\eta]$ or M_w. Therefore, primary particles endure this treatment unchanged.

After prolonged ageing crosslinking obviously becomes strong enough to withstand shearing forces. Accordingly the redissolvable fraction de-

creases with increasing ageing time and crosslinking continues in the insoluble microgel agglomerates.

At $-30°C$ under N_2 or O_2 ageing occurs very slowly and remains constant for many months (Table XII).

The lower and upper sizes of microgel agglomerates at the border of solubility could be estimated from the change of $[\eta]$ on ageing. After 6 h ageing the M_w increases from 33.1×10^{-6} to 86.8×10^6. The higher M_w represents an average microgel agglomerate, which is still just soluble. If the molecular mass distribution is allowed for, an upper limit of $M_w = 150 \times 10^6$ is obtained for soluble microgel agglomerates. This corresponds to agglomerate particles consisting of 5—6 primary microgel particles.

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