

Preparation of Amide and Amine Groups Containing Copolymers of Methyl Methacrylate and their Performance in Solid Polymer Composites

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SUMMARY:

Methyl methacrylate (MMA) was copolymerized with acrylamide, *N*-methylacrylamide, *N,N*-dimethylacrylamide, 1-vinyl-2-pyrrolidone, 4-vinylpyridine, and 2-dimethylaminomethyl methacrylate in 1,4-dioxane solution at 65 °C, using AIBN as initiator, to yield copolymers with comonomer contents between about 5 and 50 mole-%. The monomer reactivity ratios were evaluated. The copolymerizations are in general non-azeotropic and non-ideal. The amine group containing comonomers are preferentially incorporated in relation to MMA, but MMA is preferentially incorporated in relation to the amide group containing comonomers. The average molecular weights of the copolymers, with the exception of the *N,N*-dimethylacrylamide copolymer, decrease with increasing comonomer concentration, especially in the case of the amine group containing comonomers. The increasing content of amide and amine group containing monomeric units in the copolymers influences the adsorption of the polymers on an iron oxide red pigment, the dispersion stability, as well as the adhesion of the polymer coatings on steel plates and their corrosion protection.

Introduction

Composite materials of polymers and solids, such as organic coatings, show outstanding mechanical and durability properties. These materials have two interfaces, first the "inner" interface between the dispersed solid particles (of pigments and fillers), and second the interface between the coating and the substrate underneath. The interactions between the components are of physical nature (dispersion forces, dipol-dipol forces, hydrogen bridges) causing adsorption of the polymers on the solid particle surfaces and adhesion of the coating layer on the substrate surface. The adsorbed layer on the solid particle stabilizes the solid particles dispersion against flocculation. A good adhesion on the substrate is necessary to prevent corrosion of the substrate.

Attempts have been made to improve the interaction between the pigment or filler particles and the polymeric binders and hence the paint properties by chemically linking the polymer and solid particles together by polymerization reactions carried out at the solid particles surface^{1–3)}, by the reaction of chemically active groups of the polymers and the solid surfaces^{4–6)}, or by composing the polymer structure to have anchoring units, which attach the polymers to the solid surfaces^{7–11)}. Especially copolymers containing polar and non-polar sequences in a random or in a block-like arrangement are well adsorbed on solid particle surfaces from solution by the preferential interaction of the polar units, consisting e.g. of ester, amide, amine,

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carboxyl or hydroxyl groups, with polar groups at the solid surfaces, e.g. hydroxyl groups on metal oxides like silica or inorganic pigments^{5,6}.

Nitrogen containing groups are known to anchor polymers effectively on solid surfaces due to the formation of strong hydrogen bridging links. A series of random copolymers of methyl methacrylate (MMA) with varying amide and amine group containing comonomers and varying comonomer contents were prepared. The influence of these copolymers on adsorption and adhesion was studied, depending on the chemical structure of the comonomers and of the number of the *N*-containing groups. As comonomers were chosen: acryl amide (AAm), *N*-methylacrylamide (MAAm), *N,N*-dimethylacrylamide (DMAAm), 1-vinyl-2-pyrrolidone (VPO), 4-vinylpyridine (4VP), and 2-dimethylaminoethyl methacrylate (DMAMM).

This paper specially deals with the preparation of the copolymers by radical polymerization reactions, their characterisation and outlines the influence of the polymer constitution on the adsorption on an iron red pigment and on colloidal stability as well as on the formation of coating layers and their adhesion on steel substrates.

Experimental Part

Preparation of the copolymers

Methyl methacrylate (MMA) and the amide and amine groups containing comonomers, as well as solvents and precipitants, were of p.a. quality and applied without further purification to the formation of the copolymers in quantities of about 100 g.

The initiator, AIBN, was recrystallized from ethanol. The radical polymerization reactions were carried out in solution at 65 °C under a nitrogen atmosphere. In order to achieve higher degrees of conversion without altering the monomer composition during polymerization due to the preferential consumption of one of the monomers, a special technique was applied: a solution of the monomers and initiator in half the amount of solvent was prepared and added at ambient temperature over an extended period of time (6 h) to the second half of solvent stirred at reaction temperature. Thereafter, the reaction was kept along for an additional period of time (about 40 to 90 min) which was limited by the beginning increase in viscosity of the reaction mixture. The polymers were isolated by precipitation and purified twice by reprecipitation from solution (see Tab. 1). Yields were determined gravimetrically, and ranged from about 25 to 40% with the exceptions shown in Tab. 1, which summarizes the reaction conditions for the preparation of the copolymers.

The copolymer composition was calculated from the nitrogen content which was determined experimentally by micro elemental analyses (see Tab. 2).

Molecular weight determination

The molecular weights of the copolymers were determined in 1,4-dioxane solution (2,5 g/dm³) using gel permeation chromatography in combination with low angle laser light scattering analysis (GPC unit with 10³, 10⁴ and 10⁵ Å μ -styragel columns and a differential refractometer, KMX-6, of Chromatix Co.) which gave the molecular weight distribution on the basis of the absolute weight-average molecular weight of each GPC elution fraction and the number-, weight- and z-average molecular weights and the polydispersity index of the sample by calculation¹².

Adsorption experiments

The adsorption of the polymers on α -iron oxide (iron oxide red pigment, pigment red 101, with a specific surface area of 11,4 m²/g, measured by adsorption of nitrogen at 77 K with an areameter of Ströhlein Co.) was performed from solution of 2-ethoxyethyl acetate (ethylglycol acetate) at polymer concentrations of 0,5 to 20% by weight. In order to break down pigment agglomerates, the pigment was dispersed for half an hour in the polymer solution using a vibrational perl mill and glass beads of 3 mm diameter in a one to one ratio by weight related to the pigment dispersion.

The amount of adsorbed polymers was determined by the change in density of the polymer solution, measured after separation of the pigment by centrifugation. Density measurements were carried out with a density measuring cell, DMA 601, along with a density meter, DMA 60, Quarz-Biegeschwinger Dichtemeßgerät, of Heraeus/Paar.

Preparation of polymer films and determination of paint properties

Paint films of the polymers on bare steel plates were prepared from ethylglycol acetate solution containing 30% by weight of the polymer. Wet films were applied on solvent cleaned plates using a drawing bar and physically dried by evaporation of the solvent under a standard atmosphere (23 °C, 50% relative humidity) over a period of one week. The dry film thicknesses were 25 ± 5 μ m.

Paint films containing the iron oxide red pigment at a pigment volume concentration of 10% were prepared similarly, following dispersion of the pigment in the polymer solution according to the procedure described above.

The strength of adhesion of the paint films on the steel plates was measured by a pull-off test method^{13, 14}, indicating the force needed to remove the paint film from the substrate by means of a cylindrical steel test specimen glued onto the paint film.

The resistance of the paint covered steel plates to corrosion was tested in a salt spray test chamber according to the conditions described in DIN 50021 (5% solution of sodium chloride at 35 °C) and evaluated as the area corroded after 24 h duration. The corroded areas of the panels were determined by means of an automatic image analysing system (omnicon alpha 500, of Bausch & Lomb Co.).

Scanning electron micrographs of the particle distribution of the iron oxide pigment from cross cuts of the paint films were prepared after embedding the film into a resin for cutting the cross-section of ion etching of the cross cut area¹⁵.

Colour measurements of the iron oxide red pigmented paint films were carried out with a tristimulus colourmeter, and colour differences were calculated according to DIN 5033.

Results and Discussion

Copolymerization of MMA and amide and amine groups containing comonomers

Copolymerization: The radical copolymerization of MMA and acrylamide (AAM), *N*-methylacrylamide (MAAM), *N,N*-dimethylacrylamide (DMAM), 1-vinyl-2-pyrrolidone (VPo), 4-vinylpyridine (4-VP), and 2-dimethylaminoethyl methacrylate (DMAMM) was carried out in solution using dioxane (toluene in the case of 4-vinylpyridine) as solvent capable of dissolving the copolymers prepared. Azobisisobutyronitrile (AIBN) was used as initiator. The solution of the monomers containing the initiator was continuously added to the reaction mixture during the polymerization, thus feeding new monomers to substitute for consumed monomers during copolymer formation.

This method conveniently allows to polymerize to higher yields, and to maintain the monomer feed ratio initially chosen for a desired copolymer composition. As summarized in Tab. 1, yields obtained for the copolymerization of MMA and the various comonomers at different monomer feed ratios range between about 25 and 40%. Copolymerizing MMA with acrylamide or 4-vinylpyridine at higher comonomer concentrations, however, resulted in precipitating the copolymer during the course of polymerization and caused an increase in yield to 75 and/or decrease in yield to about 15%, respectively.

The monomer feed ratios were chosen according to monomer reactivity ratios for the copolymerization of MMA and amide and amine groups containing comonomers reported in literature¹⁶⁾, in order to achieve comonomer contents in the copolymers varying from about 5 to 50 mole-%.

The composition of the copolymers prepared from MMA and the amide and amine groups containing comonomers, as calculated from their nitrogen content, is summarized in Tab. 2. The copolymers can be classified into groups with comonomer contents ranging from about 3 to 6, from about 8 to 12, from about 14 to 25, and from about 30 to 54 mole-%.

The monomer reactivity ratios for the copolymerization of MMA and the amide and amine groups containing comonomers were evaluated from the initial monomer feed ratios and the copolymer compositions calculated according to the method of Fineman and Ross^{17,18)}. Fig. 1 shows that the values fit well straight lines. The monomer reactivity ratios for MMA (r_1) and the amide and amine groups containing comonomers (r_2) are summarized in Tab. 3. The data indicate that the monomer reactivities of the amide group containing comonomers to copolymerize with MMA are generally quite different from that of the amine group containing comonomers.

The ratios $r_2:r_1$, relating to the ratio of the rates by which either the comonomers or MMA are added to the growing polymer radical are smaller than unity in the case of the amide group containing comonomers, and are bigger than one in the case of the amine group containing comonomers. The latter are obviously preferred to MMA, and MMA to the first, as far as the rate of incorporating is concerned. Thus, a rank of order for the rate of incorporation of the comonomers into copolymers with MMA may be established as following: DMAMM > 4VP > AAm > MAAM > DMAAM > VPO, which relates to the ability of the *N*-containing substitutes to stabilize the growing species in the radical polymerization reaction, compared to the stabilizing ability of the ester group of MMA.

The copolymers of MMA and the amide and amine groups containing comonomers except DMAMM are formed by non-azeotropic and non-ideal copolymerization reactions according to their products $r_1 \cdot r_2$ smaller than 1. DMAMM has an azeotropic point at about 90 mole-% in the copolymerization with MMA. The product of the monomer reactivity ratios for MMA and acrylamide being bigger than unity indicates that these monomers are more likely incorporated into the copolymer in a block-like manner. The behaviour of the amide and amine groups containing comonomers to copolymerize with MMA is illustrated in the copolymerization diagram of Fig. 2.

Tab. 1. Radical copolymerisation of MMA with amide and amine groups containing comonomers at 65°C using AIBN (0,261 mole-%) as initiator

Comonomer	Copolymer	Solvent	Amount of monomers ^{a)} in mole	Solvent/mo- nomer ratio ^{b)} in ml/mole	Precipitant	Reaction time		Yield in %
						I ^{c)} in h	II ^{d)} in min	
AAM	PAAM-1	Dioxane	2,2	230	Methanol ^{e)}	6	70	35,8
	PAAM-2	Dioxane	2,2	230	White spirit/methanol	6	70	34,4
	PAAM-3	Dioxane	2,2	230	White spirit/methanol	6	70	41,2
	PAAM-4	Dioxane	1,0	435	Dioxane/acetone ^{e)}	6	70	75,0 ^{f)}
MAAm	PMAAm-1	Dioxane	2,0	230	White spirit	6	50	31,9
	PMAAm-2	Dioxane	2,0	230	White spirit	6	50	35,2
	PMAAm-3	Dioxane	2,0	230	White spirit	6	50	39,9
	PMAAm-4	Dioxane	1,5	230	Diethyl ether	6	50	26,4
DMAAm	PDMAAm-1	Dioxane	2,0	230	White spirit	6	50	31,0
	PDMAAm-2	Dioxane	2,0	230	White spirit	6	50	33,0
	PDMAAm-3	Dioxane	2,0	230	White spirit	6	50	35,1
	PDMAAm-4	Dioxane	2,0	230	White spirit	6	50	32,7
VPO	PVPO-1	Dioxane	2,0	230	White spirit	6	40	33,0
	PVPO-2	Dioxane	2,0	230	White spirit	6	40	29,8
	PVPO-3	Dioxane	2,0	230	White spirit	6	40	27,9
	PVPO-4	Dioxane	2,1	230	White spirit	6	40	23,8
4VP	P4VP-1	Toluene	2,0	230	Chloroform	6	90	32,9
	P4VP-2	Toluene	2,0	230	Chloroform	6	90	26,9
	P4VP-3	Toluene	2,0	230	Chloroform	6	90	20,8
	P4VP-4	Toluene	2,0	230	Chloroform	6	90	14,2 ^{f)}
DMAMM	PDMAAMM-1	Dioxane	2,0	230	White spirit	6	40	31,1
	PDMAAMM-2	Dioxane	2,0	230	White spirit	6	40	31,5
	PDMAAMM-3	Dioxane	2,0	230	White spirit	6	40	31,8
	PDMAAMM-4	Dioxane	1,5	230	White spirit	6	40	33,4
(MMA) ^{g)}	(PMMA) ^{g)}	Dioxane	2,0	230	White spirit	6	50	30,8

a) Composition of monomer mixture, cf. Tab. 2. b) In monomer solution added to the equivalent amount of solvent at reaction temperature. c) Addition of monomer solution to solvent. d) Additional stirring time. e) Solvent extraction instead of precipitation. f) Precipitation of copolymer in reaction mixture after about 1 h of reaction. g) Homopolymerization of MMA.

Tab. 2. Composition of copolymers obtained by copolymerizing MMA with amide and amine groups containing comonomers

Comonomer	Copolymer	Comonomer content in feed in mole-%	Nitrogen content in copolymer in %	Comonomer content in copolymer in mole-%
AAm	PAAm-1	9,9	0,71	3,60
	PAAm-2	16,9	1,50	7,61
	PAAm-3	31,9	2,88	14,61
	PAAm-4	50,5	6,82	34,61
MAAm	PMAAm-1	3,5	0,48	2,90
	PMAAm-2	9,7	1,39	8,45
	PMAAm-3	17,5	2,24	13,60
	PMAAm-4	45,0	4,89	29,60
DMAAm	PDMAAm-1	9,7	0,64	3,93
	PDMAAm-2	18,4	1,21	7,47
	PDMAAm-3	40,2	2,93	18,18
	PDMAAm-4	66,7	6,32	39,16
VPO	PVPo-1	20,7	1,01	6,09
	PVPo-2	36,9	1,82	11,05
	PVPo-3	58,0	3,09	18,80
	PVPo-4	88,3	7,32	44,45
4VP	P4VP-1	3,0	0,69	5,27
	P4VP-2	6,3	1,42	10,66
	P4VP-3	18,5	3,53	26,50
	P4VP-4	47,0	7,19	53,97
DMAMM	PDMAMM-1	2,5	0,50	5,61
	PDMAMM-2	6,0	1,07	12,02
	PDMAMM-3	11,0	1,84	20,65
	PDMAMM-4	35,0	4,13	46,35

Molecular weight: The molecular weights of the copolymers of MMA, the amide and amine groups containing comonomers, as well as of the MMA homopolymer, which was prepared in a similar manner, were determined by a combined gel permeation chromatography and low angle laser light scattering analysis, giving the absolute weight average molecular weights of each GPC fraction. The copolymers as well as the MMA homopolymer show a relatively strong increase in the cumulative weight fraction with increasing molecular weight in all cases indicating a rather narrow molecular weight distribution. Tab. 4 summarizes the z -, weight- and number-average molecular weights calculated from the molecular weight distributions. Rather small differences between the weight-average and the number-average molecular weights lead to rather small polymolecularity indices (\bar{M}_w/\bar{M}_n) - 1 ranging between about 0,3 and 0,55. Considering these values, one has to remind that the polymolecularity index obtained by combined low angle laser light scattering and GPC analysis normally is less than the true value because of the finite resolution of the GPC

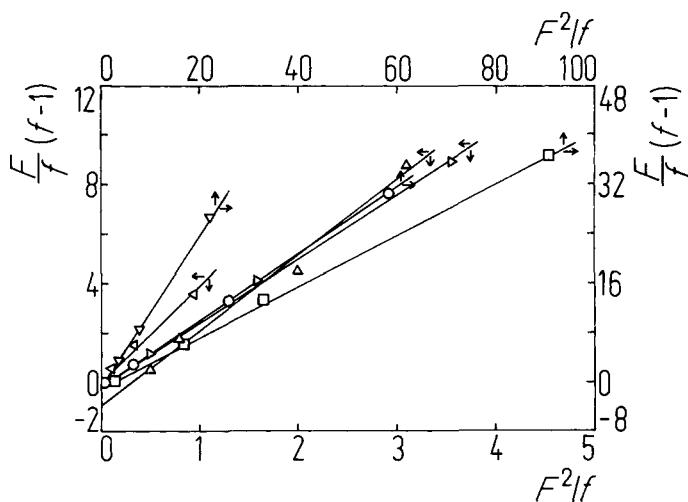


Fig. 1. Evaluation of monomer reactivity ratios. Fineman and Ross²⁷⁾ plots for the copolymerization of MMA (index 1) with AAm (Δ), MAAm (∇), DMAAm (\triangleright), VPo (\triangleleft), 4VP (\circ) and DMAMM (\square)*)

Tab. 3. Monomer reactivity ratios of MMA and amide and amine groups containing comonomers in radical copolymerization

Comonomer	Monomer reactivity ratios ^{a)}		r_2/r_1	$r_1 \cdot r_2$
	r_1 ^{b)}	r_2 ^{c)}		
AAm	$3,050 \pm 0,274$ ($2,55 \pm 0,40$)	$0,982 \pm 0,090$ ($2,45 \pm 0,35$) ^{d)}	0,322	2,995
MAAm	$1,202 \pm 0,110$	$0,178 \pm 0,025$	0,148	0,214
DMAAm	$2,650 \pm 0,100$ ($2,04 \pm 0,11$)	$0,218 \pm 0,017$ ($0,51 \pm 0,07$) ^{d)}	0,082	0,578
VPo	$3,963 \pm 0,048$ ($4,70 \pm 0,50$)	$0,023 \pm 0,111$ ($0,005 \pm 0,05$) ^{e)}	0,006	0,091
4VP	$0,543 \pm 0,025$ ($0,58 \pm 0,04$)	$1,050 \pm 0,020$ ($0,77 \pm 0,02$) ^{f)}	1,934	0,570
DMAMM	$0,416 \pm 0,010$	$0,963 \pm 0,015$	2,315	0,401

a) Polymerization in dioxane at 65°C (4VP: in toluene at 65°C).

b) Referring to MMA.

c) Referring to the comonomers.

d) In dioxane at 70°C.

e) In bulk at 50°C.

f) In bulk at 60°C.

*) Abbreviations; AAm: acrylamide, MAAm: *N*-methylacrylamide, DMAAm: *N,N*-dimethylacrylamide, VPo: 1-vinyl-2-pyrrolidone, 4VP: 4-vinylpyridine, DMAMM: dimethylaminoethyl methacrylate.

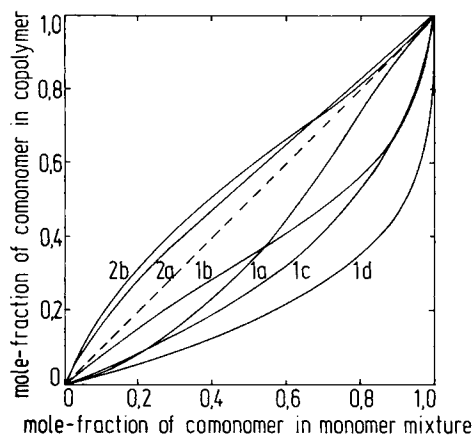


Fig. 2. Copolymerization diagram, copolymer composition in relation to comonomer ratio, for MMA and AAm (1a), MMA and MAAm (1b), MMA and DMAAm (1c), MMA and VPo (1d), MMA and 4VP (2a), MMA and DMAMM (2b)

Tab. 4. Average molecular weights of the copolymers of MMA with amide and amine groups containing comonomers and polymolecularity

Comonomer	Copolymer	Average molecular weight			Polymolecularity index $\bar{M}_w/\bar{M}_n - 1$
		\bar{M}_z	\bar{M}_w	\bar{M}_n	
AAm	PAAm-1	210 000	165 000	123 000	0,345
	PAAm-2	204 000	157 000	110 000	0,429
MAAm	PMAAm-1	221 000	151 000	97 000	0,552
	PMAAm-2	208 000	140 000	96 000	0,467
	PMAAm-3	181 000	123 000	84 000	0,461
	PMAAm-4	114 000	78 000	51 000	0,533
DMAAm	PDMAAm-1	224 000	173 000	125 000	0,382
	PDMAAm-2	210 000	160 000	109 000	0,470
	PDMAAm-3	209 000	166 000	121 000	0,364
	PDMAAm-4	220 000	168 000	118 000	0,421
VPo	PVPo-1	199 000	159 000	119 000	0,338
	PVPo-2	188 000	147 000	110 000	0,331
	PVPo-3	200 000	157 000	110 000	0,420
	PVPo-4	125 000	98 000	72 000	0,362
4VP	P4VP-1	148 000	114 000	79 000	0,452
	P4VP-2	121 000	93 000	66 000	0,403
	P4VP-3	86 000	68 000	52 000	0,314
	P4VP-4	45 000	38 000	30 000	0,260
DMAMM	PDMAMM-1	176 000	127 000	98 000	0,297
	PDMAMM-2	142 000	106 000	78 000	0,365
	PDMAMM-3	72 000	53 000	41 000	0,291
	PDMAMM-4	54 000	42 000	32 000	0,321
(MMA) ^{a)}	(PMMA) ^{a)}	233 000	182 000	125 000	0,451

^{a)} Homopolymer, prepared under the same conditions.

column¹⁹). The weight average molecular weights of the MMA homopolymer and of the MMA copolymers containing small amounts of the amide and amine groups containing comonomers are in the order of about 150000 to 170000.

Copolymers of MMA and amide and amine groups containing comonomers: As can be derived from Tab. 4, the average molecular weights decrease with increasing comonomer content in the copolymers. Since the radical polymerization of methyl methacrylates is known to be terminated by disproportionation reactions of the growing species, even at temperatures between 60 and 70°C, chain transfer reactions either to the comonomers or to the comonomer units in the copolymer are assumed to cause the decrease of the molecular weights. Fig. 3 indicates the chain transfer activity of the various comonomers by a plot of the reciprocal degree of polymerization

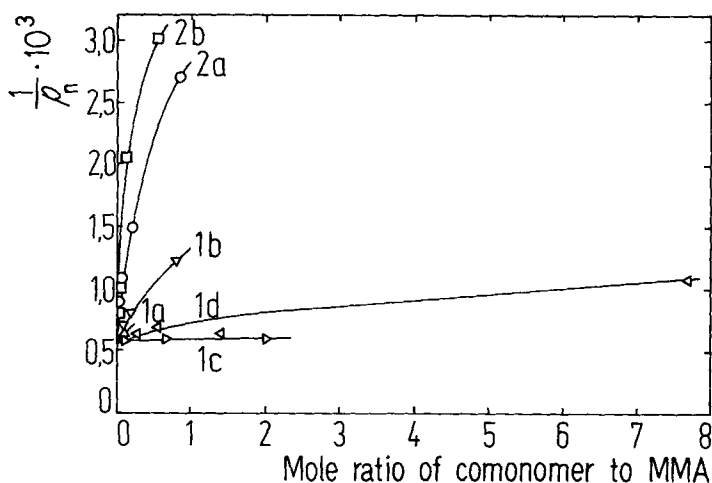


Fig. 3. Reciprocal degree of polymerization ($1/P_n$) of copolymers in relation to comonomer concentration in monomer mixture for copolymerizing MMA with AAm (Δ), MAAm (∇), DMAAm (\triangleright), VPo (\blacktriangleleft), 4VP (\circ), and DMAMM (\square)

versus the comonomer concentration in the reaction mixture. The tertiary amides *N,N*-dimethylacrylamide and 1-vinyl-2-pyrrolidone are obviously not or less influencing the molecular weight of the copolymers, whereas an increasing chain transfer activity is observed in the case of acrylamide, *N*-methylacrylamide and especially in the cases of the tertiary amines, 4-vinylpyridine and 2-dimethylaminoethyl methacrylate. The chain transfer reactions may occur by hydrogen abstraction from methyl groups in the case of the 2-dimethylaminoethyl methacrylate monomer units, or in α -position in the polymeric backbone in the case of the 4-vinylpyridine monomer unit, the radicals created being stabilized by the tertiary amine group. The smaller chain transfer activity of the amide group containing monomer units may be due to the smaller stabilization effect of the radicals by the electron withdrawing amide group.

Adsorption of the polymers on iron oxide and colloidal stability of the pigment dispersion

The adsorption of the copolymers prepared and of a MMA homopolymer from solution on iron oxides (Pigment red 101) is performed at varying polymer concentrations (from 0,5 to 17,5 and 25% by weight) using ethylglycol acetate as solvent. This solvent was chosen because it dissolves the MMA homopolymer as well as most of the copolymers with various contents of the amide and amine groups containing comonomers.

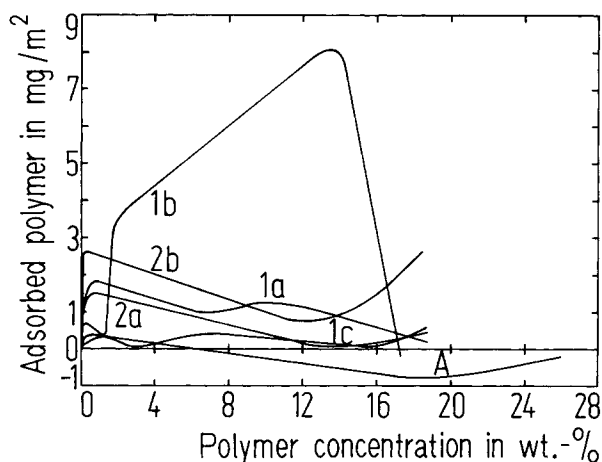


Fig. 4. Adsorption isotherms for the adsorption of a MMA homopolymer (A) and copolymers of MMA with AAm (PAAm-I; 1a), MAAm (PMAAm-I; 1b), DMAAm (PDMAAm-I; 1c), 4VP (P4VP-I; 2a), and DMAMM (PDMAMM-I; 2b)

Fig. 4 shows the adsorption isotherms of the copolymers of MMA and amide and amine groups containing comonomers and a technical MMA homopolymer. Except for 1-vinyl-2-pyrrolidone the materials contain only about 5 mole-% of the comonomers. The iron oxide was dispersed according to the procedure described in the Exptl. Part. At smaller polymer concentrations of about 1–2% by weight, the adsorbed amount on the iron oxide increases at increasing concentration of the polymers in the solutions. An adsorption layer on the pigment surface is formed consisting of polymer and solvent needed for solvating the adsorbed polymer molecules, the composition of which remains constant with increasing polymer concentration according to the observations of Rehaček²⁰⁾ for the polymer adsorption on solid particles at high polymer concentrations. This results in a decrease of the apparent amount of adsorbed polymer with increasing polymer concentration, yielding a straight line of the adsorption isotherm since that measure for the polymer adsorption is obtained from changes in the concentration of the polymer solution. The intersection of the

straight line with the abscissa indicates that at that point no change in the polymer concentration occurs by the adsorption of the polymer. The polymer concentration of the solution is equal to the concentration of the polymer in the adsorption layer at the pigment particle surface. The amount of truly adsorbed polymer can be evaluated, according to Rehaček²⁰⁾, by extrapolating the straight line of the adsorption isotherm to the ordinate.

Fig. 4 reveals that the copolymers of MMA and amide and amine groups containing monomers are adsorbed at higher amounts than the corresponding MMA homopolymer, which is adsorbed on the iron oxide pigment from ethylglycol acetate solution to 0,4 mg/m² of the iron oxide (value of truly adsorbed polymer). Data evaluated after Rehaček²⁰⁾ in Tab. 5 demonstrate the amide group containing

Tab. 5. Amount of copolymers of MMA and amide and amine groups containing comonomers and of a MMA homopolymer adsorbed from ethylglycol acetate solution on iron oxide red pigment (according to Rehaček²¹⁾)

Comonomer	Copolymer	Amount of adsorbed polymer in mg/m ²
—	PMMA ^{a)}	0,41
AAm	PAAm-1	1,83
MAAm	PMAAm-1	0,76
DMAAm	PDMAAm-1	0,49
	PDMAAm-2	2,69
	PDMAAm-3	7,82
	PDMAAm-4	8,38
4VP	P4VP-1	1,63
DMAMM	PDMAMM-1	2,61
	PDMAMM-2	3,79
	PDMAMM-3	3,60
	PDMAMM-4	3,85

a) Technical MMA homopolymer, molecular weight, by viscosity, of about 60000 to 70000.

copolymers are adsorbed at moderately higher amounts (0,5 to 1,8 mg/m²), but the amine group containing copolymers at 4 to 6 times larger amounts (1,6 to 2,6 mg/m²). This can be explained by a stronger interaction of the copolymers, when compared to the MMA homopolymer, with the iron oxide surface via more polar binding forces or hydrogen bridging links between the hydroxide groups of the surface and the amide and amine groups of the copolymers. Larger amounts of adsorbed polymer in the case of the amine group containing copolymers may be caused by the larger ability of the amine groups to form hydrogen bridges, when compared to amide groups, due to the higher electron-density of their nitrogen atoms.

As can be seen from Tab. 5 the amount of truly adsorbed polymer depends on the number of amide or amine groups and in addition on the kind of the copolymerized adhering groups. The amount of adsorbed polymer increases in the case of *N,N*-di-

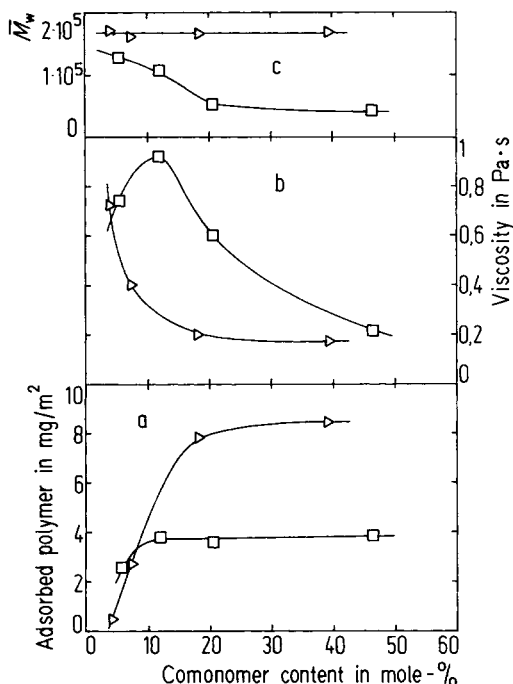


Fig. 5. Characteristics of copolymers of MMA with DMAAm (\triangleright) and DMAMM (\square) at various comonomer contents. a) Adsorption on iron oxide red pigment from ethylglycol acetate solution at a concentration of 20 wt.-%. b) Viscosity of copolymer solutions in ethylglycol acetate at 17,5 wt.-%. c) Molecular weight (\bar{M}_w) in ethylglycol acetate solution by light scattering

methylacrylamide copolymers with increasing comonomer content, but soon reaches a constant value in the case of the 2-dimethylaminoethyl methacrylate copolymers. This behaviour is illustrated in Fig. 5 which shows both the polymer molecular weight and the viscosity of the polymer solution in ethylglycol acetate (at a concentration of 17,5% by weight) depending on the comonomer content. At constant molecular weights, the viscosity of the dimethylacrylamide copolymer decreases strongly with increasing comonomer content, whereas the viscosity of the 2-dimethylaminoethyl methacrylate copolymers, while the molecular weight is decreasing, is first increasing, than decreasing with increasing comonomer content. This behaviour may indicate, that solvation of the polymer molecules by the solvent, ethylglycol acetate, is altering with increasing contents of the nitrogen containing groups on the polymer.

Consecutively it may be concluded that the adsorption of the copolymers from solution on iron oxide is not only primarily determined by the interactions of the amide or amine groups of the polymer and the hydroxide group of the iron oxides, but is secondarily influenced by the solvation of the polymer molecules in the solvent. On this basis the following observations may be explained: the increase of adsorbed polymer with increasing comonomer content and minima and maxima of the apparent adsorbed polymer in the adsorption isothermes with increasing polymer concentration. Stronger polymer-polymer interaction in the poor solvent ethylglycol acetate via polar or hydrogen bonding forces between the amide or amine groups lead to an adsorption equilibrium, in which the attachment of the polymer molecules to the solid surface is preferred to solvation of the polymer in solution.

Dispersing behaviour

The interaction of the polymers in solution with the solid particles determines the dispersion of the solid in the fluid as well as the colloidal stability of the dispersed particles against flocculation. This can easily be shown by investigating the settling behaviour of pigments in the polymer solutions. The dispersed iron oxide pigment rapidly settles down to form large sediment volumes in solutions of the MMA homopolymer, but settling times increase and sedimentation volumes become smaller when solutions of the amide and amine groups containing copolymers are used to disperse the pigment. According to this qualitative measure for the colloidal stability of dispersions, the methyl methacrylate homopolymer is not able to prevent the pigment particles from flocculation, but a polymer stabilizes the pigment dispersions against flocculation if amide or amine groups containing comonomers are incorporated into its chain. This behaviour may be explained by restricting the direct interaction of the pigment particles, leading to flocculation, by the interaction of the surface hydrogen bond forming and containing groups of the copolymers.

Fig. 6 shows iron oxide pigment particles by means of scanning electron micrographs in a polymer film, where the size of the pigment particles formed by agglomeration or flocculation and their distribution over a thin film are fixed by evapora-

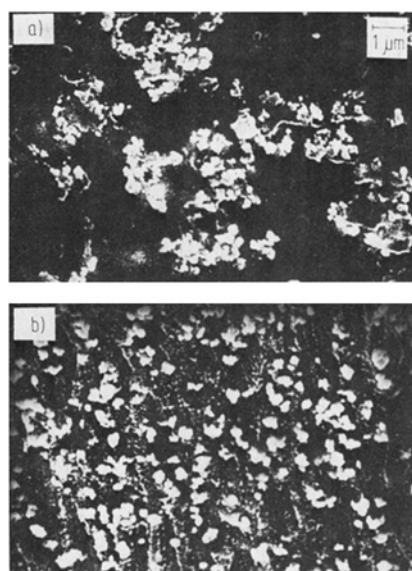


Fig.6

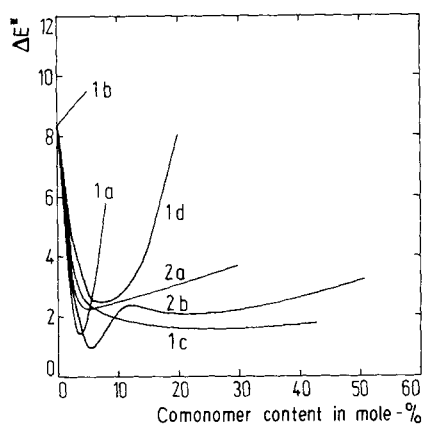


Fig. 7

Fig. 6. Scanning electron micrographs of iron oxide red pigment dispersed in PMMA (a) and a copolymer from MMA and 5 mole-% DMAMM (b)

Fig. 7. Colour differences ΔE^* of films pigmented with iron oxide red pigment before and after rub out test. Films prepared from ethylglycol acetate solutions of copolymers of MMA with AAm (1a), MAAm (1b), DMAAm (1c), VPo (1d), 4VP (2a), and DMAMM (2b)

tion of the solvent. Large flocculates formed by primary pigment particles as well as pigment-free volumes in the paint film indicate poor dispersion stability as the iron oxide pigment is dispersed in MMA homopolymer (Fig. 6a), whereas smaller pigment particles and even primary particles are almost uniformly distributed over the paint film using a methyl methacrylate/2-dimethylaminoethyl methacrylate copolymer with a comonomer content of about 5 mole-% as a film forming polymer (Fig. 6b).

Some characteristics such as hiding power, transparency and colour depend on the pigment particle distribution in the paint film, i.e. on the degree of flocculation of the pigment particles. The difference between flocculated or deflocculated pigment dispersion may be used to characterize the influence of the polymer constitution on the polymer/polymer interaction.

The flocculation of a partly flocculated paint can be altered by rubbing the paint film during the drying period, when applied at a time when the increasing viscosity due to the evaporation of the solvent starts to immobilize pigment particle distribution (rub out test). By this test small colour differences between rubbed and not rubbed paint areas indicate good stabilization of pigment particles to flocculation, whereas large colour differences illustrate strong flocculation of pigment dispersion. Colour differences from rub out tests are shown in Fig. 7 for paints containing iron oxide pigment which are prepared from either MMA homopolymer or from the amide and amine groups containing copolymers of MMA at various comonomer concentrations. The strongly flocculating activity of the MMA homopolymer, as seen in Fig. 6a, results in a high colour difference value of more than 8. Small contents of either amide or especially amine groups of about 5 to 10 mole-% in the copolymer cause a decrease of the pigment particles flocculation, as indicated by colour difference values decreasing to about 1 to 2. A quite different activity of the various amide and amine groups containing copolymers to contribute to colloidal stability was observed when the comonomer contents are increased. A rather good stabilization of the pigment particle against flocculation is maintained by the amine group containing and the dimethylacrylamide group containing copolymers, whereas the acrylamide and 1-vinyl-2-pyrrolidone containing copolymers with higher comonomer contents obviously cause a strong flocculation of the pigment particles. In addition, the methylacrylamide copolymer caused, even at small comonomer contents, a large colour difference (see Fig. 7).

Since the acrylamide and methacrylamide copolymers containing higher contents of the comonomer units are not well soluble in the commonly used solvent ethylglycol acetate at the relatively high polymer concentrations (17,5 wt.-%) applied for the preparation of the paints, it may be assumed that a poor solubility of these amide group containing copolymers, even at lower comonomer contents, may be responsible for the insufficient colloidal stability of the pigment dispersions, as it was assumed above for the height of the amounts of adsorbed polymer.

This is in agreement with the theory of the steric stabilization of dispersions by adsorbed polymer layers^{21, 22}. Accordingly, a good solubilization of the adsorbed polymer provides stabilization of the solid particle against flocculation, whereas a poor solvation causes flocculation of the particles.

Adhesion

Adhesion of the polymers to steel plates and anti-corrosive efficiency were examined to evaluate the influence of the polymer constitution on the interaction with a steel substrate. Coatings of the amide and amine groups containing copolymers of MMA and of a technical MMA homopolymer (pigment-free) on degreased steel plates were prepared by drawing the polymer solutions in ethylglycol acetate, at a concentration of 17,5 wt.-%, and evaporation of the solvent to yield polymer films of about 30 μm layer thickness.

The adhesive strength of the polymer films on the steel substrate was measured by the force needed to remove the coating from the steel plates by means of a test specimen glued onto the coating film. Fig. 8 shows the adhesive strength for the MMA homopolymer and the *N*-containing copolymers depending on the comonomer content. The MMA homopolymer exhibits a relatively moderate adhesive strength about 4,6 N/mm² when compared to values of the adhesion of paint films prepared from alkylmelamine or epoxy resins to phosphated or galvanized steel, which range from 7 to 10 N/mm² ²³). The adhesive strength is increased when 4-vinylpyridine- or 2-dimethylaminoethyl methacrylate units are incorporated into the MMA polymer and exceeds a value 1,5 times larger than that of the adhesion of the MMA homopolymer at comonomer contents larger than 30 mole-%. This is to explain by increased binding forces between the polymer via its amine groups and the steel surface, certainly consisting of a thin iron oxide or iron oxihydrate layer.

Dimethylacrylamide- and 1-vinyl-2-pyrrolidone containing copolymers tend to increased adhesive strength at small comonomer contents, but at higher comonomer contents the adhesive strength decreases again. Acrylamide and methylacrylamide are

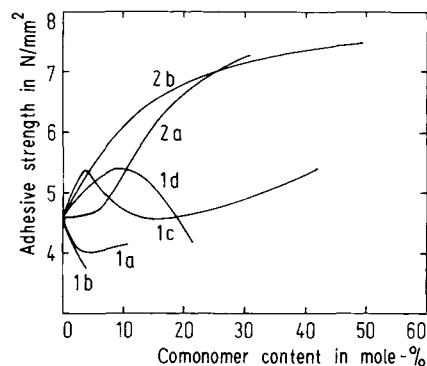


Fig. 8

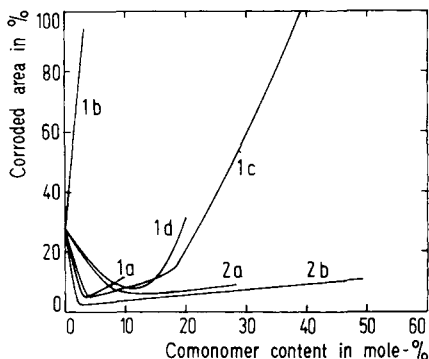


Fig. 9

Fig. 8. Adhesive strength of films on degreased steel plates in relation to comonomer content for copolymers of MMA with AAm (1a), MAAm (1b), DMAAm (1c), VPo (1d), 4VP (2a), and DMAMM (2b)

Fig. 9. Corroded area of degreased steel plates coated with films from copolymers of MMA with AAm (1a), MAAm (1b), DMAAm (1c), VPo (1d), 4VP (2a), and DMAMM (2b). Corrosion test DIN 50021 (5% NaCl solution, 35°C, 24 h)

decreasing the adhesive strength even at low comonomer contents. This behaviour is not well understood, but may be seen in close connection with the state of solvation of these copolymers in ethylglycol acetate, which is assumed to prefer the polymer/polymer interactions as mentioned above.

Corrosion protection

Since adhesion of the coating films is known to be one of the responsible factors for anti-corrosive protection of steel substrates by organic coatings²⁴⁾, it seems to be interesting how the amide and amine groups containing comonomer units influence the anti-corrosive efficiency of coatings prepared thereof.

Fig. 9 represents the results of salt spray tests after 24 h test duration according to test conditions of DIN 50021. Coating films on degreased steel plates were prepared from the amide and amine groups containing copolymers and from the MMA homopolymer. The percentage of the corroded area is taken as a measure.

The corroded area is about 30% in the case of the MMA homopolymer as a film forming material, but decreases when the amide and amine groups containing comonomers are incorporated into the polymer at contents up to 5 or 10 mole-% except for methylacrylamide. This may be explained by the increasing adhesive strength of the polymer films to the steel substrate as described above. The corroded areas increase, however, with larger comonomer contents, especially in the case of the 1-vinyl-2-pyrrolidone (1d), *N*-methylacrylamide (1b) and *N,N*-dimethylacrylamide copolymers (1c), where in some cases severe rust was observed.

Beyond a particular content of the *N*-containing comonomers the polymers do not protect the steel substrate against corrosion. Large amounts of polar and hydrophilic amide or amine groups obviously facilitate the diffusion of water and oxygen through the polymer films to the interface with a steel substrate and facilitate the corrosion processes.

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