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Synthesis of Novel Amphiphilic Copolymers by Acid-Mediated Free-Radical Polymerization and Solution as Well as Particle-Stabilization Properties

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Summary: Hydrophobically modified copolymers with different content of hydrophobic/hydrophilic segments can be synthesized by free radical copolymerization of acrylic acid (AA) with isobutene (IB) in the presence of strong Brönsted acids such as trifluoracetic acid (TFA). By variation of the comonomer ratio, the copolymer composition and its hydrophilic/hydrophobic properties can be adjusted. The copolymerization of AA and IB in the presence of TFA leads to copolymers which formally consist of periodic sequences of $[\text{IB-AA}]_X$ randomly interrupted by homo sequences of $[\text{AA}]_Y$. This reflected from the linear dependence of the glass transition temperature with the [IB-AA] unit mole fraction while no direct correlation with the overall IB or AA mole fraction is given. The [IB-AA] sequences are relatively hydrophobic due to the IB unit, while [AA] sequences represent the hydrophilic part. Aqueous solutions of the periodic copolymers are characterized by specific and concentration dependent viscosities which are attributed to intermolecular association phenomena of alternating $[\text{IB-AA}]_X$ sequences. The copolymers have been shown to be potential stabilizers of titanium dioxide particle dispersions in water as has been established by electrokinetic sonic amplitude and sedimentation measurements. These data are again correlated with the periodic chain structure. A conformational model of $[\text{AA}]_Y$ anchor segments as "trains" and $[\text{IB-AA}]_X$ "loops" and "tails" is proposed.

Introduction

In recent years, amphipolar copolymers have been of increasing interest as stabilizes for particulate systems especially as far as emulsions and dispersions are concerned [1, 2]. One area of application is the stabilization of pigments: By using amphipolar polymers, both the electrostatic and steric stabilization mechanisms can become effective [3, 4]. The resulting electrosteric stabilization involves the deposition of the amphipolar copolymer on the pigment surface and thereby generating a coated pigment of a different charge density than the pristine pigment, and at the same time forming a shell of solvated macromolecules around the pigment [5, 6]. These different stabilization mechanism are schematically shown in Figure 1.

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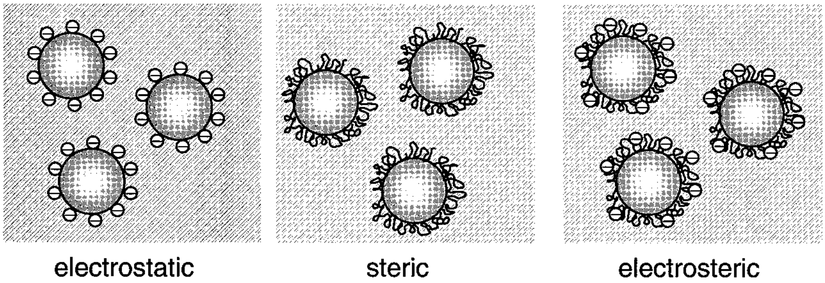

Figure 1. Schematic of the different stabilization mechanism of pigments.

Amphipolar copolymers which are suited to stabilize pigments may be random copolymers or graft and block copolymers. Whereas amphipolar or amphiphilic block copolymers consisting of a hydrophobic and hydrophilic block have already been studied in literature [7, 8] little is known about the efficiency of amphipolar graft copolymers or statistical copolymers in the stabilization of, e.g., aqueous pigment dispersions. In previous studies we have investigated a series of block- and graft copolymers based on polystyrene and polyacrylic acid [9, 10]. It has been shown that the type and extent of copolymer-pigment interaction varies distinctly with the constitution of the copolymer, and also with the hydrophobic/hydrophilic ratio of building blocks (charge density) within the copolymer. Based on electrokinetic sonic amplitude (ESA) measurements as well as spectroscopic and transmission electron microscopical studies some insights in the copolymer pigment-interaction and the stabilization mechanism of these block and graft copolymers have been obtained [10].

In this paper we report our studies on a series of linear amphipolar copolymers based on isobutene (IB) and acrylic acid (AA). The synthesis of these copolymers is based on an acid-mediated copolymerization of isobutylene and acrylic acid in the presence of trifluoracetic acid (TFA) as complexing agent. It has already been shown that the free radical copolymerization of olefins with acrylic comonomers in the presence of acids (Lewis acid or Brönsted acid) gives strictly alternating copolymers (cf. [11, 12]), and that the regularity in the alternating sequences is related to the alteration of the comonomer reactivity ratio of the acrylic comonomer by the interaction with the acid; for the example of acrylonitrile (AN) as acrylic comonomer, the degree of alternation, i.e., the ratio of the alternating acrylonitrile-olefin sequence to acrylonitrile homo sequences could be varied by the TFA/AN or the olefin/AN ratio [13].

Based on these findings we have investigated the copolymerization of acrylic acid and isobutylene in the presence of trifluoracetic acid in view of the potential of such copolymers which can be considered as hydrophobically modified polyelectrolytes as polymeric stabilizers for aqueous pigment dispersions. The copolymers were characterized for their thermal bulk and aqueous solution viscosity properties, and with regard to their adsorption mechanism and stabilizing efficiency onto titanium dioxide pigments.

Experimental Section

The copolymers were synthesized by free radical copolymerization of isobutene (IB) and acrylic acid (AA) with trifluoroacetic acid (TFA) as complexing agent and cyclohexylperoxy bicarbonate (CHCP) as initiator in dichloromethane solvent at 40 °C. The mole ratio TFA/AA was 1/1. The copolymerization was carried out in analogy to the procedure which has been described for the copolymerization of acrylonitrile (AN) and ethane (ET) (cf. [13]); further details will be given elsewhere [14].

The copolymer composition was obtained by ^{1}H- and ^{13}C-NMR analysis (Bruker Avance 250).

Molar mass determination was done by gel permeation chromatography (GPC); in order to avoid polyelectrolyte effects, the polyelectrolytes were converted to the methyl esters by esterification of the carboxyl groups with diazomethane in a polymer analogous reaction (cf. [13]). Polystyrene and polymethymethacrylate standards were used for calibration.

Differential scanning calorimetry (DSC) analysis was done with a Perkin Elmer Iris Instrument; calibration was carried out with Indium and water; both heating and cooling rates were 20 K per minute.

The experimental conditions for the electrokinetic sonic amplitude (ESA) measurements and the sedimentation analysis were carried out as described elsewhere (cf. [10]).

Results and Discussion

Copolymerization

The acid-mediated copolymerization of an electron donor comonomer such as isobutylene (IB) with a polar electron acceptor comonomer such as acrylic acid (AA) in the presence of trifluoracetic (TFA) acid gives a periodic copolymer consisting of the alternating [IB-AA] and $[AA]_Y$ homo sequences as represented in the reaction scheme Figure 2.

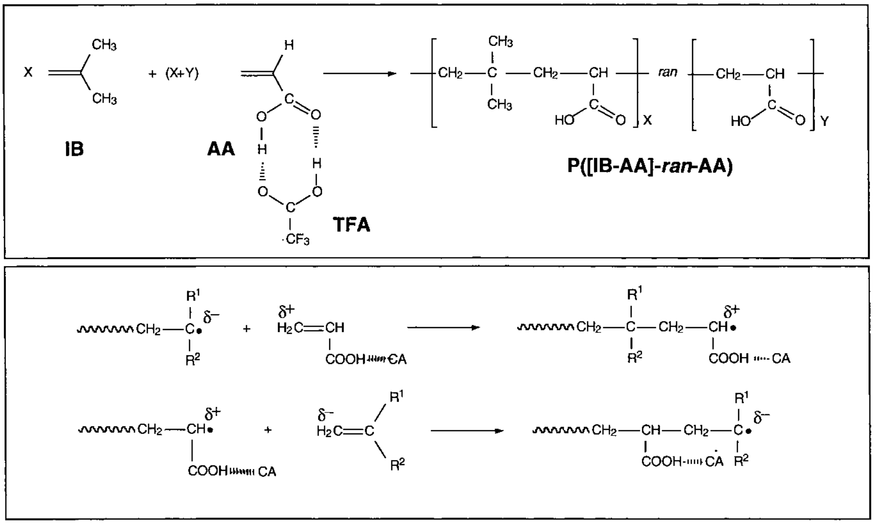

Figure 2. Acid mediated copolymerization of isobutene (IB) and acrylic acid (AA) in the presence of trifluoroacetic acid (TFA) and reaction mechanism of olefin (R^1, R^2 = H, alkyl) and AA with complexing agent (CA).

The complexation of the acrylic monomer by the acid lowers the electron density of this acceptor monomer as well as the acceptor monomer radical chain end; this is responsible for the increased reactivity of the complexed AA towards the electron-rich olefin, i.e. IB chain end and, also, for the increased reactivity of the electron donor comonomer IB to the complexed AA radical chain end. Thus, from a mechanistic point of view, the usual cross-over propagation takes place in the copolymerization of complexed acrylics with non-conjugated olefins (cf. [11, 12]).

The copolymerization parameters as determined by the Fineman-Ross-method are r_{IB}= 0,003 for IB and r_{AA} = 1,59 for AA. It can be inferred from these reactivity ratios that the homo addition of the IB comonomer is neglectably small, i.e., there are no polyisobutylene sequences to be expected in the polymer. However, $[AA]_Y$ homo sequences cannot be avoided. This means, that copolymers with a nearly alternating structure are only obtained with a large olefin excess in the feed. This is evident from the data given in Table 1.

Table 1. Periodic copolymers of isobutene (IB) and acrylic acid (AA) (P([B-AA]-*r*-AA)) synthesized by free radical copolymerization of AA and IB with trifluoro acetic acid (TFA) as complexing agent for the acrylic monomer according to [11] with dicyclohexylperoxy bicarbonate (CHPC (1 mole-%)) as initiator in CH_2Cl_2 as solvent at 40 °C.

Copolymer	**$[AA]_0/[IB]_0$**	**TFA:AA**	**Yield**	**Mn$^{a)}$**	**Mn/Mw**	**% AA$^{b)}$**	**% IB$^{b)}$**	**[IB-AA]$^{b)}$**
	mole/l	**mole/mole**	**%**	**g/mole**		**mole-%**	**mole-%**	**mole-%**
PAA-1	--	--	90.7	2.000	1.75	100	0	0
PAA-2	--	--	85.0	200.000	1.88	100	0	0
P([B-AA]-*r*-AA)-1	2:1	1:1	67.3	55.000	2.59	82	18	22
P([B-AA]-*r*-AA)-2	1:1	1:1	75.1	46.000	2.71	71	29	41
P([B-AA]-*r*-AA)-3	1:1	1:1	69.8	87.400$^{*)}$	2.47	69	31	45
P([B-AA]-*r*-AA)-4	1:3	1:1	73.2	105.000$^{*)}$	2.05	63	37	58
P([B-AA]-*r*-AA)-5	1:5	1:1	72.5	56.000	2.27	60	40	67
P([B-AA]-*r*-AA)-6	1:10	1:1	95.6	74.000$^{*)}$	2.23	54	46	84
P([B-AA]-*r*-AA)-7	1:15	1:1	71.3	64.000	2.83	52	48	92

a) M_n from GPC analysis in THF with PMMA standards

b) M_n from GPC analysis in DMA with PS standards

c) Percentage of AA, IB and [IB-AA] as determined by ^{1}H-NMR in methanol-d^4

These results show that it is possible to tailor the polyelectrolyte structure with regard to the mole fraction of alternating $[IB\text{-}AA]_X$ sequences and $[AA]_Y$ homo sequences. In this context, it is interesting to note that the resulting copolymers cannot be regarded as random copolymers since the IB comonomer is only built into the polymer chain within the alternating sequence.

If we consider the repeat unit of the alternating sequence which consists of the [IB-AA] moiety as a new monomer, these copolymers may be described as random copolymers consisting of two different repeat units, i.e., the [AA] and [IB-AA] unit.

Thermal Properties

The above picture of a copolymer with periodic sequences, i.e., a random copolymer of the [IB-AA] and [AA] repeat unit, is confirmed from the variation of the glass transition temperatures Tg with composition.

The DSC traces of periodic copolymers of different comonomer composition together with the DSC trace of the pure polyacrylic acid (PAA) are shown in Figure 3. The DSC trace of the pure polyisobutene (PIB) homopolymer with a T_g at -73 °C is not shown. The graph in Figure 4 demonstrates that the variation of T_g with the IB content is fairly well described by the Gibbs-DiMarzio equation, where $x_{[AA]}$ and $x_{[IB\text{-}AA]}$ represent the mole fractions of the homo polyads of [AA] and the alternating polyads of [IB-AA] with the T_gs of the corresponding PAA homo polymer and the strictly alternating P([IB-AA]) copolymer.

The calculation of the glass transition temperature by assuming a random AA/IB and copolymer structure by applying the rule of mixing of the two comonomers as, e.g., in the form of the Fox Equation (and by using the T_gs of the AA and IB homopolymers) gives figures which are much too low. This means that, for a copolymer with the alternating [IB-AA] sequence, the alternatingly incorporated IB constitutional unit has a stiffening effect on the polymer rather than a softening effect as would be expected by comparison with the T_g of pure PIB.

This is a further proof of the general view that an alternating unit is a new constitutional unit and that such copolymers exhibit unusual properties which are quite different from corresponding random copolymers which do not contain the alternating hetero sequence.

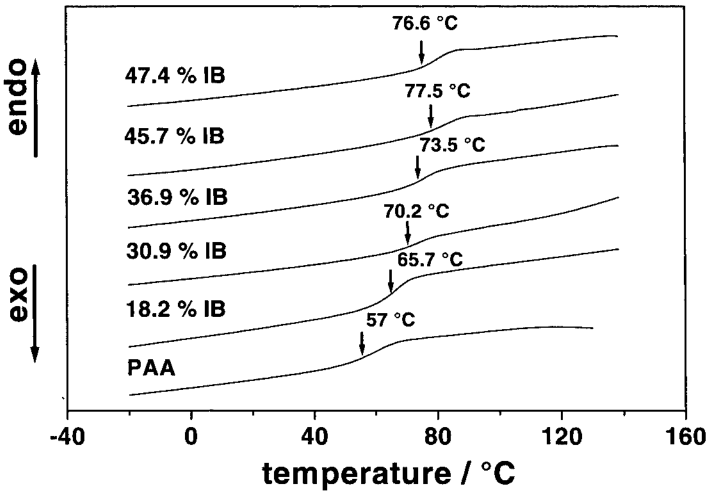

Figure 3. DSC traces of poly(acrylic acid) (PAA) and periodic acrylic acid (AA)/isobutene (IB) copolymers P([IB-AA]-*ran*-AA); mole-% IB in the copolymer indicated.

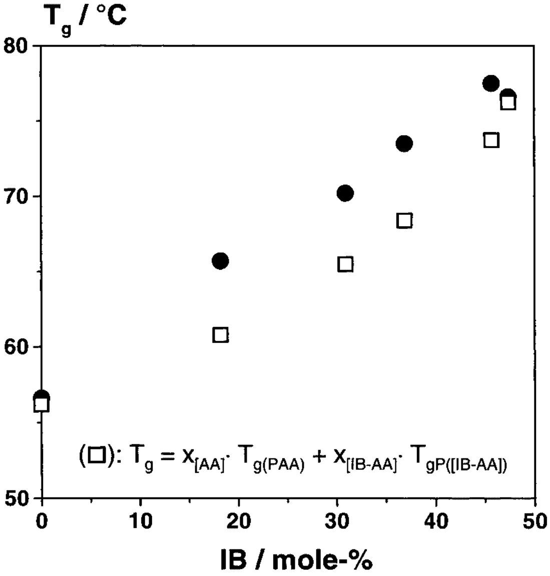

Figure 4. Dependence of the glass transition temperature T_g of acrylic acid (AA)/isobutene (IB) copolymers with periodic [IB-AA] and [AA] sequences; ●: experimental data; □: calculated figures with $T_{g(PAA)} = 56$ °C and $T_{gP([IB\text{-}AA])} = 78$ °C.

As has already been mentioned above, these copolymers with periodic alternating [IB-AA] sequences and $[AA]_Y$ homo sequences can be considered as hydrophobically modified polyacrylic acid. Due to the IB unit, the alternating sequence is less hydrophilic than the $[AA]_Y$ homo sequence. This means that, in analogy to the well-known behavior of, e.g., hydrophobically modified polyacrylamide (cf. [15]) the AA/IB-copolymers with periodic sequences should exhibit special concentration dependent viscosity features, and, as the consequence of the carboxylic group, also pH dependent phenomena.

The change of the reduced viscosity with pH and the correlation with the HCl-titration curve reveals the pH-controlled polyelectrolyte conformation (Figure 5). The viscosity is almost independent from pH in the alkaline region, but drops rapidly with increasing protonation of the polyelectrolyte below pH 8. This is explained by the shrinkage of the coil which is due to both the decrease of the charge density of the polymer chain and the decrease in solubility with decreasing degree of dissociation [16].

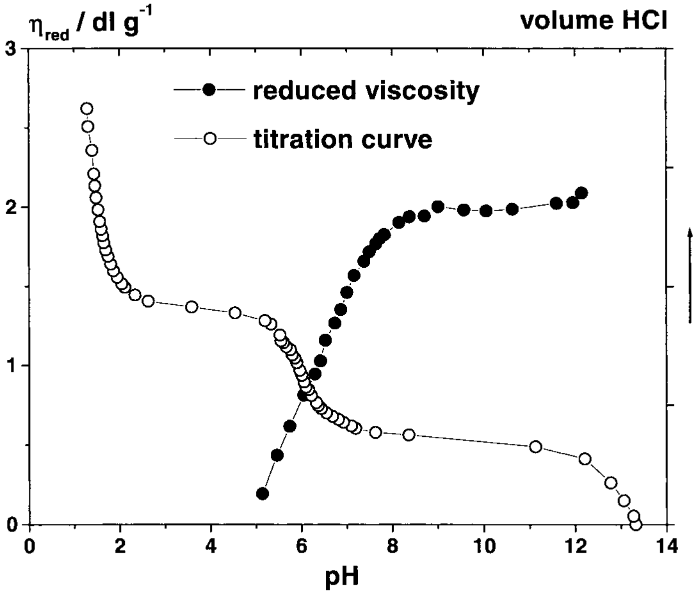

Figure 5. pH Dependence of the reduced viscosity η_{red} of P([IB-AA]-*r*-AA) containing 22 mole-% [IB-AA] units and titration curve (with HCl) starting from the alkaline region; polyelectrolyte concentration: 2.235 g/dl.

The change in viscosity with decreasing pH increases for a given copolymer concentration with the mole fraction of alternating sequences, and is also most pronounced for higher concentrations (Figure 6).

The comparison of the data of P([IB-AA]-*r*-[AA]) with 22 mole-% [IB-AA] units at concentrations 0.4 g/dl and 2.235 g/dl show that the viscosity change with pH is less pronounced if the copolymer concentration is below the critical overlap concentration ($c^* = 1.93$ g/dl at pH 13) as compared to the situation when the overlap concentration is exceeded.

The effect of the degree of hydrophobicity of the polyelectrolyte macromolecule with regard to the mole fraction of alternating sequences on the pH dependent viscosity is reflected from the comparison of the curves obtained with P([IB-AA]-*r*-[AA]) of 22 and 59 mole-% alternating sequences: For the given copolymer concentration of 2.235 g/dl, in the case of the copolymer with the lower mole fraction of the alternating sequences, the critical overlap concentration of 1.93 g/dl is not yet reached, whereas in the case of the copolymer with 59 mole-% alternated sequences, the critical overlap concentration (2.17 g/dl) is almost reached.

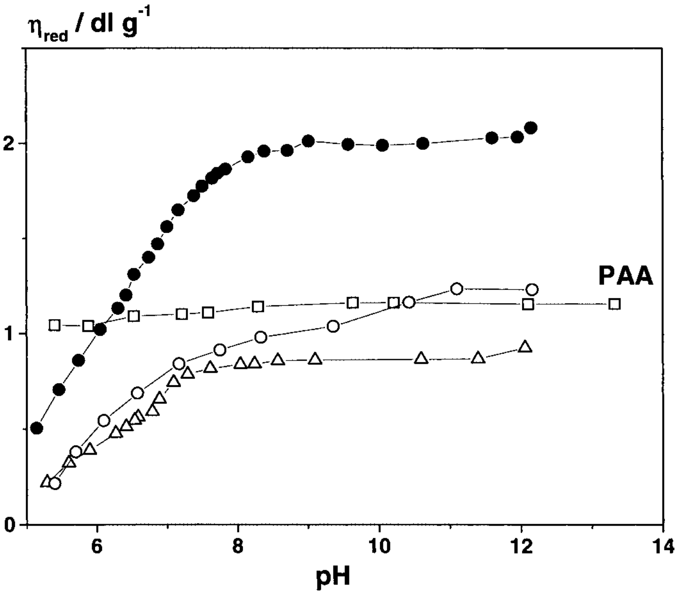

Figure 6. pH Dependence of the reduced viscosity η_{red} of P([IB-AA]-*r*-AA) for copolymers of different content of AA-IB units and at different concentrations; □: PAA (2.235 g/dl); ●: P([IB-AA]-*r*-AA) of 22 mole-% [IB-AA] units (2.235 g/dl); Δ: P([IB-AA]-*r*-AA) of 59 mole-% [IB-AA] units. (2.235 g/dl); O: P([IB-AA]-*r*-AA) of 22 mole-% [IB-AA] units (0.4 g/dl).

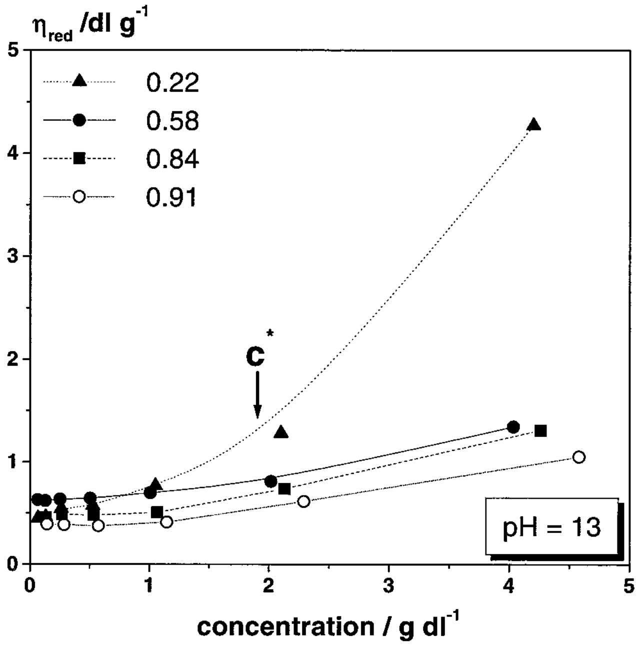

Figure 7. Change of the reduced viscosity η_{red} with P([IB-AA]-*r*-AA) copolyelectrolyte concentration in aqueous solution (pH 13) for copolymers with different mole fraction x of relatively hydrophobic [IB-AA] sequences; x is given in the figure with the symbols.

This means that besides the macromolecule contraction with decreasing degree of dissociation, also the effects of intramolecular interactions (below the critical overlap concentration) and intermolecular interactions between the relative hydrophobic [IB-AA] sequences (becoming effective when the overlap concentration is approached) have to be considered.

The effect of the copolymer composition (hydrophobic alternating sequences) on the change of viscosity with copolymer concentration in aqueous solution (pH 13) is illustrated in Figure 7. Whereas copolymers with a relatively high fraction of hydrophobic alternating sequences show a slight, but almost linear increase of the reduced viscosity with concentration, the copolymer with only 22 mole-% hydrophobic sequences exhibits a distinct increase in viscosity for concentrations above 2 g/dl, i.e. when the critical overlap concentration is exceeded. This thickening behavior is similar as observed for, e.g., hydrophobically modified poly(acrylamide).

Copolymer-Pigment Interactions

Detailed information about the interaction of the synthesized copolymers, e.g., about the adsorption/desorption phenomena were obtained by applying the electrokinetic sonic amplitude (ESA; cf. [17, 18]). The ESA measurement is suited to determine the dynamic mobility μ_d (mobility in an alternating field); the zeta potential and the particle size can be obtained from the data analysis. For the sake of better comparison, the reduced dynamic mobility $\mu_{0,5MHz}/\mu_0$ is used, which relates the dynamic mobility measured for the pigment in the aqueous polyelectrolyte solution ($\mu_{0,5MHz}$) to the dynamic mobility of the pigment alone in the polymer-free aqueous dispersion.

The dependence of the reduced dynamic mobility $\mu_{0,5MHz}/\mu_0$ on the relative polymer concentration is depicted in Figure 8 for a series of periodic copolymers with varying mole fraction of alternating [IB-AA] repeat units in the copolymer; for comparison, the corresponding curves for PAA (two different molecular weights) are also included.

A general feature observed with all polyelectrolytes is that a limiting value of the reduced mobility is reached with increasing polymer concentration; this value is called saturation concentration (SC) and is given by the intercept of the extrapolated lines of the initial slope and final slope as schematically shown in Figure 8 for the copolymer with 60 mole-% AA rsp. 67 mole-% of alternating [IB-AA] units.

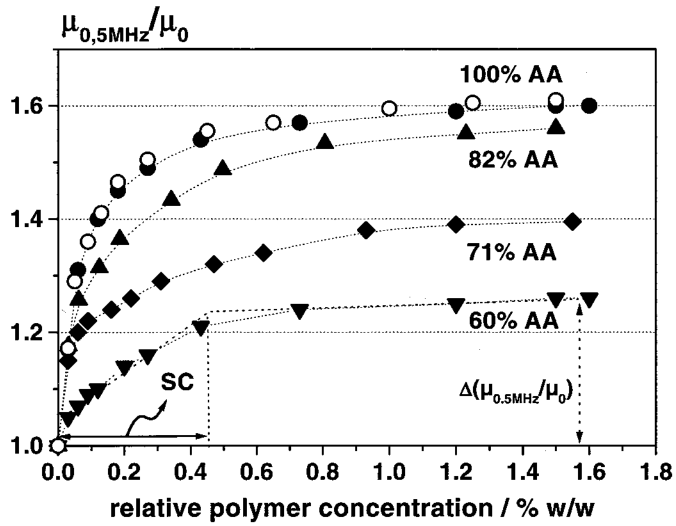

Figure 8. Reduced dynamic mobility from ESA measurements for TiO_2 dispersions (1 % v/v) under addition of poly(acrylic acid) and periodic acrylic acid (AA)/isobutene (IB) copolymers P([IB-AA]-*r*-AA) with different ratio of acrylic acid in the copolymer; the total AA mole-% of the (co)polymer is indicated for the corresponding curves.

The steepness of the curve in the low polymer concentration regime as well as the final value of the dynamic mobility increase with decreasing amount of alternating [IB-AA] units in the copolymer. The saturation concentration as obtained for pure PAA corresponds to a complete coverage of the pigment surface by polyacrylic acid in the so-called train-conformation [10]. The total amount of adsorbed PAA on the pigment is about 0.23 % w/w or 0.014 mg/m^2 which agrees well with literature data [19]; with these figures, a surface area occupied by each carboxylic group of 0.88 nm^2 is obtained (calculation based on the BET-surface of 17 m^2/g and the molecular weight of 71.05 g/mole for an ionized acrylic monomer repeat unit of flatly adsorbed PAA).

The increase in the saturation concentration for the copolymers with increasing incorporation of [IB-AA] alternating units which goes along with a decrease of the final reduced dynamic mobility is coupled to a change from the train-conformation (obtained with PAA) to the loop and tail conformation. This can be understood with the picture that the $[AA]_Y$ homo sequences act as anchoring points on the pigment surface whereas the somewhat less hydrophilic $[IB\text{-}AA]_X$ sequences form a spacially more extended adsorption layer with loops and tails. In the same way as the copolymer is depleated on $[AA]_y$ homo sequences, the amount of totally adsorbed copolymer increases if one assumes a similar number of carboxylic interacting groups on the pigment surface; because of the less ionic character of the IB-containing alternating $[IB\text{-}AA]_x$ sequences as compared to the pure $[AA]_Y$ homo sequences, the reduced dynamic mobility which is predominantly controlled by the overall pigment surface charge density is also reduced.

The model of polyelectrolyte-pigment interaction of polyacrylic acid as contrasted to the periodic copolymers is illustrated in Figure 9.

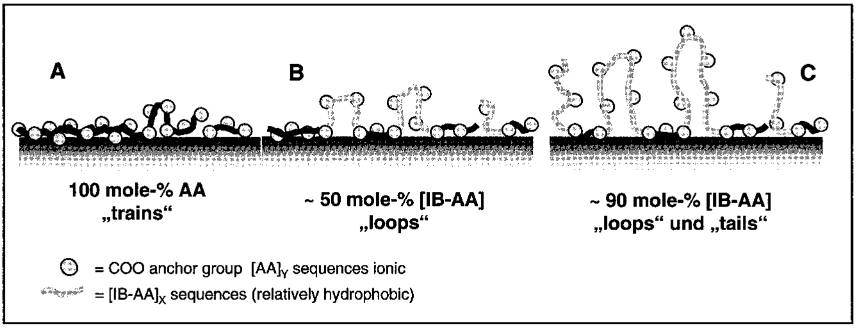

Figure 9. Dependence of the copolyelectrolyte conformation of acrylic acid (AA)/isobutene (IB) copolyelectrolytes P([IB-AA]-*r*-AA) from the content of relatively hydrophobic alternating [IB-AA] sequences: change from train for pure PAA (A) to loop (B) and loop and tail conformation (C) for the periodic copolymers.

The PAA adsorption on the titanium dioxide pigments corresponds to the situation A as shown in Figure 9. The formation of loops and tails with increasing content of alternating sequences (decrease of $[AA]_Y$ homo sequence anchor units) is illustrated by the schematic B and C. In this model, for the copolymers with long alternating $[IB\text{-}AA]_X$ hetero sequences, a thermodynamically stable situation is approached by the interaction of the carboxylic groups of the hydrophilic $[AA]_Y$ homo sequences with the pigment surface whereas the less hydrophilic alternating $[IB\text{-}AA]_X$ sequences point to the water-phase.

The variation of the saturation concentration SC as well as the relative increase of the dynamic mobility (difference between the dynamic mobility with and without added copolymer) is shown in Figure 10. The comparison of the variation of these quantities with the total amount of AA in the copolymer (Figure 10a) and the amount of alternating [IB-AA] units in the copolymer (Figure 10b) shows that a linear correlation is only obtained for the dependency on the [IB-AA] units.

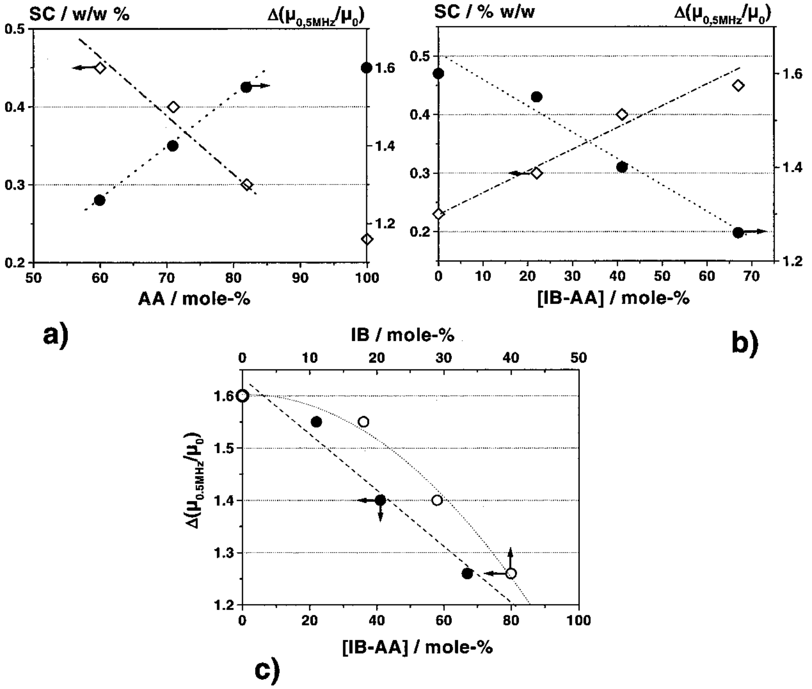

Figure 10. Variation of the saturation concentration SC and of the relative increase of the dynamic mobility $\Delta(\mu_{0.5MHz}/\mu_0)$ in relation to the total amount of AA (Figure 10a), of alternating [IB-AA] units in the copolymer (Figure 10b), and a comparison of the dependence of $\Delta(\mu_{0.5MHz}/\mu_0)$ from the amount of $[IB\text{-}AA]_x$ and the overall IB-comonomer content (Figure 10c).

This clearly reflects the effect of the special constitution of the copolymer chain on the interaction with the pigment surface in that the characteristics of these copolymers with regard to their alternating sequences are crucial and that these copolymers have nothing in common with random copolymers. This is further confirmed by Figure 10c where again a distinct deviation from the linear relationship obtained for the $[IB\text{-}AA]_x$ dependence is seen in the dependency on the overall IB-comonomer content.

The results of sedimentation measurements for 0.5 % v/v TiO_2 dispersions containing 0.5 % w/w polyelectrolyte with regard to the pigment concentration are given in Figure 11. It is evident that a stabilization effect of the polyelectrolytes on the titanium dioxide dispersion is obtained in all cases.

The plotting of the sedimentation velocity in Figure 12 which is obtained from the slope of the change of the sedimentation height (see Figure 11) vs. the molar content of alternating [IB-AA] units in the copolymers reveals that there is an optimum composition of this periodic copolymer with regard to the stabilization of the pigment dispersion.

The fact that a periodic copolymer with about 40 mole-% [IB-AA] alternating units shows the lowest stabilization effect, i.e. a maximum in the sedimentation velocity as compared to the pure poly(acrylic acid) (0 mole-% [IB-AA]) or the strictly alternating copolymer (100 mole-% [IB-AA]) indicates that there is an optimum balance between the electrostatic stabilization (which is the dominant factor for pure poly(acrylic acid)) and the steric stabilization.

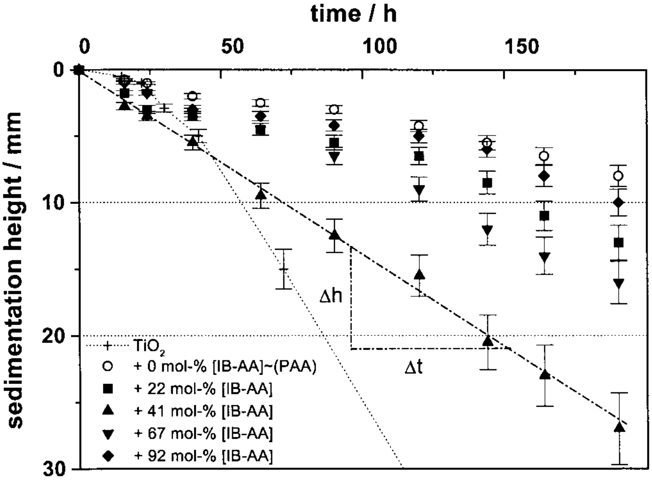

Figure 11. Sedimentation measurements of TiO_2 dispersed in aqueous media (+) and of TiO_2 dispersions (0.5 % v/v) with added poly(acrylic acid) (PAA) (○) and acrylic acid (AA)/isobutene (IB) copolyelectrolytes (P([IB-AA]-*r*-AA)) with different total amount of alternating [IB-AA] sequences.

Obviously a minimum in the electrosteric stabilization is reached for systems with $[AA]_Y$ anchor units and a certain number of loops and tails of $[IB\text{-}AA]_x$ hetero sequences; a further increase of the alternating sequences up to the limit of the alternating copolymer, which goes to the expense of the overall charge density of the copolymer coated particle but increases the contribution of steric stabilization, is again favorable for the stability of the particulate system. This situation is also visualized from the packing/conformation model of polyelectrolytes with varying content of alternating sequences as shown in Figure 9.

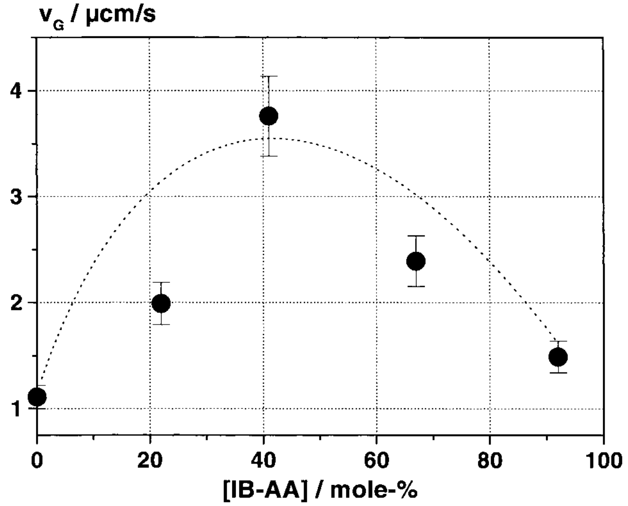

Figure 12. Sedimentation velocity (obtained from the slope of the change of the sedimentation height from Figure 11) vs. the molar content of alternating [IB-AA] units.

The assumed electrosteric stabilization mechanism is in accordance with this picture and an optimum balance between the steric stabilization contribution of the alternating sequences and the screening effect of the alternating sequences on the overall particle charge density has to be considered. The effect of the alternating sequences in such periodic copolymers on polyelectrolyte-pigment interactions will be further studied, also in comparison to amphiphilic block- and graft copolymers (cf. [10]).

Conclusions

The studies have shown that the constitution of statistical copolymers with regard to the type and amount of $[IB\text{-}AA]_x$ alternating sequences has a distinct effect on copolymer properties. Structure-properties relationships are best related to the mole fraction of alternating comonomer units rather than to the overall comonomer content; the latter would be appropriate for a true random AA/IB copolymer only. The ESA measurements have brought some insight into the particular polyelectrolyte-pigment interaction in that the anchor units are considered to be the $[AA]_Y$ homo sequences, whereas the alternating sequences point to the aqueous phase in a loop or tail conformation.

Acknowledgement

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