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CATECHOL-CONTAINING POLYMERIC MATERIALS AS SELECTIVE pH-CONTROLLED FLOCCULANTS OF ULTRAFINE AQUEOUS DISPERSIONS OF RUTILE WITH RESPECT TO ILMENITE (°)

Riassunto — Copolimeri radicalici di monomeri vinilici contenenti residui 3,4-bis(metossimetossi)fenilici o 3,4-diidrossifenilici con acido acrilico sono stati preparati e saggiati nella flocculazione selettiva di dispersioni acquose ultrafini di minerali di titanio. Le prove di sedimentazione hanno mostrato che alcuni dei copolimeri preparati aventi peso molecolare nell'intervallo 150000-350000 si comportano da ottimi flocculanti del rutilo, selettivi rispetto all'ilmenite, con azione dipendente dal pH. Un possibile meccanismo di formazione dei fiocchi viene brevemente discusso.

Abstract — Fully synthetic radical copolymers of vinyl monomers containing 3,4-bis(methoxymethoxy)phenyl or 3,4-dihydroxyphenyl residues with acrylic acid were prepared and tested for the selective flocculation of ultrafine aqueous dispersions of titanium minerals. Sedimentation tests showed that some of the prepared copolymers having molecular weight in the 150000-350000 range are excellent selective pH-dependent flocculants of rutile with respect to ilmenite. A possible mechanism for the formation of flocs is briefly discussed.

Key words — Selective flocculation, Catechol-type copolymers, Titanium minerals, Ultrafine dispersions.

Introduction

The intensive milling of minerals requested by many mining processes produces conspicuous quantities of ultrafines with parti-

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cle sizes smaller than 20 micron, which are untreatable by conventional techniques, flotation included, and represent a considerable economic loss.

The selective flocculation through polymers of the aqueous dispersions of such ultrafines is one of the most recent and significant advances in their beneficiation, but in spite of many applications on laboratory and pilot plant scale reported in literature (Yu *et Al.*, 1987) the technique is severely limited by the lack of proper selective flocculating substances.

Searching to fill in this gap, in previous works we developed a simplified theoretical model of the structure of a polymeric flocculant (Bertini *et Al.*, 1987) and we applied it to the design and preparation of flocculants for chalcocite selective versus quartz and calcite (Bertini *et Al.*, 1986), or for rutile and ilmenite selective versus quartz (Bertini *et Al.*, 1987), or for ilmenite selective versus rutile (Bertini *et Al.*, 1990).

In this work we report on vinyl copolymers containing free or protected catechol residues able to selectively flocculate ultrafine aqueous dispersions of rutile with respect to ilmenite.

EXPERIMENTAL SECTION

Instruments

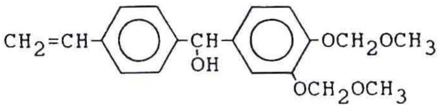
Melting points were determined on a Kofler apparatus. IR spectra were recorded on a Perkin Elmer 1330 instrument. ^{1}H-NMR spectra were run on Bruker 300 and Varian XL-100 spectrometers using tetramethylsilane as internal standard. Viscosity measurements ($[\eta]$) were performed with an Ubbelohde viscometer on dilute polymer solutions in dioxane at 25°C. Number average molecular weights ($\bar{M}_n$) were determined at 37°C in dioxane with a Knauer Membrane Osmometer or at 45°C in methanol with a Knauer Vapor Pressure Osmometer.

Minerals

Rutile (97% TiO_2) from Florida (U.S.A.) and ilmenite (51% TiO_2) from Risor (Norway) were used. Each mineral was ground wet in a porcelain mill using distilled water. The fraction with particle size lower than 15 micron was collected and used in a slurry form.

CHEMICALS

Reagents, solvents and acrylic acid were obtained from Fluka (Switzerland) and were purified according to standard procedures. Monomers 3,4-bis(methoxymethoxy)phenyl-4-styryl-carbinol (I), 3,4-bis(methoxymethoxy)phenyl-4-styrylketone (II) and 3,4-dihydroxyphenyl-4-styrylketone (III) were prepared according to POCCI *et Al.,* 1990.



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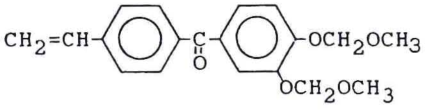

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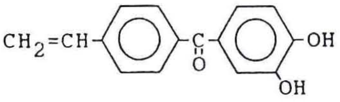

III

POLYMERS AND COPOLYMERS

General procedure:

Degassed monomers, anhydrous peroxide-free solvent and initiator were introduced in the desired ratios under nitrogen in the polymerization flask and magnetically stirred at the fixed temperature.

For monomers I and II dioxane as solvent, AIBN as initiator and 60°C as polymerization temperature were chosen. For the 1,2-diphenolic monomer III, the cyclohexanone/tri-*n*-butylborane system and a temperature of 30°C were used.

After a suitable period (2-50 h) the polymerization mixture was poured into the non-solvent, the precipitated polymer was filtered and vacuum dried overnight at room temperature. The copolymers were fractionated by partial precipitation from stirred 1% solution in a thermostatic bath at 25°C by slow addition of non-solvent as listed in Table 1.

IR and ^{1}H-NMR spectra confirmed the disappearance of the vinyl group and the presence of 3,4-bis(methoxymethoxy)phenyl residues in the copolymers of I and II and of 3,4-dihydroxyphenyl residues in the copolymers of III.

More representative polymerization and copolymerization experiments together with solubilities and fractionation solvents are reported in Table 1.

SEDIMENTATION TESTS

Experiments were carried out in 100 ml graduated cylinder with a useful depth of 185 mm. A volume of slurry corresponding to about 2 g of mineral was introduced in the cylinder, diluted with distilled water up to the 70 ml mark and treated with the prefixed volume of a 0.1% solution of polymer in aqueous 0.1N NaOH. The mixture was shaken for 5 minutes, adjusted to the desired pH with standard HCl or NaOH solutions and diluted to volume (100 ml). After shaking for 15 minutes the mixture was left to settle for such a time that in absence of polymer, at the same pH and ionic strength, the amount of the mineral still dispersed in the upper 70 ml was about 1 g or 50% of the amount used in the test. The upper 70 ml of the dispersion were siphoned off. The siphoned (70 ml) and remaining (30 ml) dispersions were separately dried to constant weight. The obtained weights, deduced of the weights of the non-volatile products as calculated from the used volumes of HCl, NaOH and alkaline polymer solution, were applied for the determinations of the flocculating power (F) and the dispersing power (D) according to the following formulas:

$$F = \frac{p_o - p}{p_o} \times 100 \qquad D = \frac{p - p_o}{p_w - p_o} \times 100$$

where

p_o = weight of the mineral contained after sedimentation in the upper 70 ml of the slurry in the absence of polymer

p = weight of the mineral contained after sedimentation in the upper 70 ml of the slurry in the experiment with the polymer

p_w = 70% of the weight of all the mineral used in the experiment with the polymer

When parallel experiments with and without polymer are performed with unequal starting amounts of the mineral, the following normalization relation for p_o was used:

TAB. 1 - *Representative polymers and copolymers prepared.*

Monomers		Mole fraction of M_1 in the feed	Reaction solvent* (ml/mol of monomers)	Time (min)	Conversion %**	Solvents	Non-solvents	Fractionation (solv./non-solv.)
M_1	M_2							
I	—	1.00	711	2820	73.1	d,e,f,g,h	a,b,c,g,i,j,l	—
I	AA	0.05	281	1020	43.3	d,g,h,k	a,b,c,e,f,i,j,l	g/b
II	—	1.00	3703	1920	41.4	d.e.g	a,b,c,i,j,k,l	—
II	AA	0.05	233	380	25.0	d,g,h,i,k	a,b,e,j,l	d/a
II	AA	0.20	741	1330	81.0	d,g,k	a,b,e,i,j,l	d/a
III	—	1.00	1296***	1440	68.5	b,d,h,i,k	a,c,e,f,j,l	—
III	AA	0.10	483***	1152	34.5	d,i,k	a,b,c,e,f,j	d/e
III	AA	0.20	516***	1620	36.8	d,i,k	a,b,c,e,f,j	d/e
III	AA	0.50	1905***	1230	52.9	h,i,k	a,b,c,d,e,f,g,j,l	i/c
—	AA	0.00	250	140	76.1	g,i,j,k,l	a,b,c,e,f	g/b

* dioxane/60°C/AIBN 0.5% by weight, unless otherwise noted.

** (total weight of recovered polymer/total weight of starting comonomer mixture) x100.

*** cyclohexanone/30°C/TBB 1% by weight.

AA = acrylic acid.

a = petrol, b = benzene, c = diethyl ether, d = tetrahydrofuran, e = dichloromethane, f = chloroform, g = dioxane, h = dimethylformamide, i = methanol, j = water, k = 0.1N NaOH, l = 0.1N HCl.

$$p_o = \frac{p_{o,u} \times p_t}{p_{o,t}}$$

where

$p_{o,u}$ = weight of the mineral contained after sedimentation in the upper 70 ml of the liquid in the experiment without polymer
$p_{o,t}$ = weight of all the mineral used in the experiment without polymer
p_t = weight of all the mineral used in the experiment with the polymer

RESULTS AND DISCUSSION

The synthesis of tailor made polymeric flocculants for titanium minerals has been carried out on the basis of a previously developed theoretical model of the structure of such flocculants accomplished by three types of chemical functions: i) functions able to interact specifically with the particle surface of the examined mineral; ii) functions showing hydrophobic properties including the paraffinic chain of the vinyl copolymer; iii) functions showing hydrophilic character dependent on pH.

Following these guidelines successfully exploited in the selective flocculation of titanium minerals with copolymers containing 3,4-methylenedioxyphenyl or 3,4-diacetoxyphenyl residues (BERTINI *et Al.*, 1990) and wishing to explore the catechol-type derivatives as functions of interaction with the mineral particle, we prepared and examined polymers and copolymers of the monomers I-III. They combine the known complexing ability of the catechol functions towards titanium ions (SOMMER *at Al.*, 1963) with the property, at least for monomers II and III, of the benzophenone system of adsorbing onto metal oxides through the two benzene rings (FRANK *et Al.*, 1984). The coupling of these two properties may result in a rather stable interaction and a wider shielding of the particle surface from water. The mineral dispersion is thus prearranged towards easier flocculation conditions. The selection of an acrylic acid type matrix for the prepared copolymers was determined by its hydrophilicity and solubility markedly dependent on pH.

Monomer I was polymerized and copolymerized with acrylic acid, but the copolymers revealed a spontaneous decrease in solubility with time, thus making these materials unsuitable as flocculants.

Most likely, as already observed in analogous systems (BERTINI *et Al.*, 1987), a crosslinking reaction consequent to ether bridge formation between two alcoholic groups in benzylic position, can be claimed as responsible of the observed behaviour.

Monomer II was synthesized and copolymerized with acrylic acid in various molar compositions, ranging from 5 to 20 mole % of II, using azobisisobutyronitrile (AIBN) as radical initiator. The obtained copolymers appeared as grainy powders characterized by a number average molecular weights in the 150000-350000 range.

Monomer III containing the unprotected diphenolic function had to be copolymerized with acrylic acid in presence of the tri-*n*-butylborane/cyclohexanone system (IWABUCHI *et Al.*, 1974), but the obtained materials had low molecular weights in the 5000-12000 range, that probably were responsible for the lack of good flocculating action.

In conclusion, among all the prepared materials, the copolymers of II resulted as the only ones useful for flocculation purposes showing fully satisfactory selective action towards rutile.

Table 2 collects the results of typical flocculation experiments with the copolymer II (0.050)/acrylic acid (0.950) having a molecular weight $\bar{M}_n = 343000$ and with a sample of polyacrylic acid (PAA) having molecular weight $\bar{M}_v = 360000$ synthesized for comparison purposes.

TAB. 2 - *Flocculating power % (F) and dispersing power % (D) of polyacrylic acid (PAA) and the copolymer II (0.050)/AA (0.950) at 50 ppm and various pH versus rutile and ilmenite.*

Polymer	pH	Rutile	Ilmenite
PAA	2.5	D 3	F 14
$[\eta] = 45.6$ ml/g*	3.0	F 2	D 10
$\bar{M}_v = 360000$**	4.5	D 25	D 99
	5.5	F 10	D 99
	7.0	D 48	D 2
	9.0	D 36	D 4
II (0.050)/AA (0.950)	2.5	F 97	D 57
$[\eta] = 107.7$ ml/g	3.0	F 89	D 87
$\bar{M}_n = 343000$°	4.5	F 1	D 93
	5.5	D 5	D 89
	7.0	D 8	D 1
	9.0	D 12	D 4

* in dioxane at 30°C.

** obtained from the relation $\log [\eta] = \log 0.076 + \log \bar{M}_v$ (NEWMAN *et Al.*, 1954).

° in dioxane at 36°C.

The lack of significant flocculation when PAA homopolymer was used, reveals the essential role of 3,4-bis(methoxymethoxy)phenyl residues in the flocculation process with the copolymer II/AA. A significant interaction can be claimed for this last polymer with the particle surface through coordinative bonds with the superficial acidic centers corresponding to crystal lattice coordination vacancies or through the formation of hydrogen bonds with the surface hydroxyl groups. Such interactions may either contribute to the binding of the copolymer onto the particle surface or produce a shielding action from water molecules with a decrease of the direct surface solvation. These allow the copolymer to acquire the control of particle-solvent and particle-particle affinities and make them dependent upon dissociation of the free carboxylic groups in the copolymer itself. When the dissociation of the carboxylic groups and their solvation are strongly depressed, as at low pH values, the particles tend to aggregate and allow crossed interactions of the copolymer molecules with the surface of different particles, then giving rise to the formation of stable flocs.

The prepared materials are flocculant in a limited pH region at acidic values and dispersant or inert in all the others. This very useful pH dependent activity allows the flocculation process to be carried out by mixing the mineral slurry and copolymer at non flocculating pH conditions and successively to be achieved by careful change of pH in such a way that flocs are formed gradually. In this way the heterogeneous system can significantly limit the inclusion of spurious particles.

As far as the copolymer composition and concentration are concerned, the experiments performed indicate that the best flocculating conditions are attained by using copolymers containing from 5 to 20 mole % of II at concentration values between 10 and 50 ppm. The molecular weight of the copolymer does not show any significant influence on the flocculation process at least in the examined range between 150000 and 350000 dalton.

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