Impact of Functional Group Distribution on the Adsorption of a Polymeric Dispersant

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Binder polymers functionalized with a small amount of polar groups satisfy both the dispersion quality of paints and the mechanical strength of coating films. For industrial-grade polydisperse dispersant polymers, functional groups are not evenly distributed among the polymer chains. The functional group distribution in polyurethane dispersant polymers was investigated by statistical estimation and an adsorption experiment. The polymeric dispersants had a broad functional group distribution and contained a significant amount of nonfunctionalized chains. By considering the existence of these ineffective chains, the dispersion behavior of the paint was more clearly explained. The described method can be a useful tool to analyze the structure and the properties of polydisperse functionalized polymers for various applications.

INTRODUCTION

Pigment dispersion in organic solvents generally depends on the steric repulsion of the adsorbed polymer layer around the particles.[1] Hence, various methods have been developed to increase the adsorbed polymer amount onto the pigment. One method introduces a polar group onto the polymer chain.[2] Polar groups, which are commonly used in dispersants and surfactants, generally show a strong affinity against hydrophilic inorganic pigment surfaces.[3,4] The dispersant polymers functionalized with a small amount of polar groups show a higher adsorption efficiency and improve the dispersion quality of paints.[5,6] Since this technique does not use smaller molecules such as surfactants, it can also satisfy the mechanical properties of the coating films. Because of these advantages, polymeric dispersants are used in high-end applications such as magnetic paints.[6]

When a dispersant polymer is used, it should be noted that industrial-grade synthetic polymers are polydisperse as a result of a random polymerization. The molecular weight distribution is a well-known polydispersity characteristic,[7,8] and a functional (polar) group distribution among the chains may also exist. In the case of low molecular weight dispersants or surfactants, all molecules generally have at least one functional group. For random copolymers, the existence of the functional group on each chain will be dominated by statistical probability. Still, if the content of the functional group or the molecular weight of the polymer is high enough, almost all polymer chains will have several functional groups. However, for dispersant polymers, the average number of functional groups per chain is generally one or two, and the average molecular weight is at most $2\sim3\times10^4$. These are practical choices to maintain the original polymer properties such as solubility in organic solvents. Under this condition, some of the chains may not have functional groups. These nonfunctionalized chains will contribute less to the adsorption and the dispersion. At the opposite end, overfunctionalized chains may exist and will cause various problems in solubility and viscosity. Hence, it is important to examine the distribution of the functional groups among the chains and its effect in the adsorption and the dispersion properties.

The adsorption behaviors of polydisperse homopolymers and end-functionalized oligomers were previously examined.[8-10] In the case of dispersant polymers, though the effectiveness of functional groups had been reported,[6] the effect of the functional group distribution was not studied. To clarify these aspects, the functional group distribution in a polyvinylchloride functionalized with sulfate anion was examined in a previous

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Table 1—Characterization of Polyurethanes

Polymer	M_w[a] (g/mol)	M_w/M_n[a]	RSO_3^-[a] (μ eq/g)	RSO_3^-[b] (μ eq/g)
A	2×10^4	2.0	0	0
B	2×10^4	2.6	30	27
C	2×10^4	2.3	60	61
D	2×10^4	2.3	90	85
E	2×10^4	1.9	150	147

(a) Supplier's data.
(b) Experimentally determined.

study.[11] In this report, the functional group distribution in polyurethane dispersant polymers containing different concentrations of sulfonate groups was investigated. The distribution was estimated by statistical calculation and a sequential adsorption experiment. The dispersion behavior of the dispersant polymers was more precisely understood by considering the functional group distribution among the chains.

EXPERIMENTAL

Materials

The dispersant polymers were commercial-grade sulfonate anion (RSO_3^-) functionalized polyester-polyurethanes with an average molecular weight of 2×10^4. The basic properties of the polymers are listed in *Table* 1. The molecular weight of the polyester chain is approximately 1×10^3. Therefore, a typical polyurethane chain consists of about 20 polyester units bound by urethane units. By mixing an RSO_3^- functionalized polyester ($M_w \sim 1 \times 10^3$, having one RSO_3^- group), the polymer contains RSO_3^- groups corresponding to the mixed amount. The exact content of the RSO_3^- group in the polymers was measured by X-ray fluorescence spectroscopy. A sample polymer was mixed with an equal amount of a polyvinylchloride as a standard material. The RSO_3^- content was determined by measuring the sulfur (S_{00}) and chlorine (Cl_{00}) peaks. The intensity of the peaks was calibrated by measuring the reference samples containing sodium dodecylbenzensulfonate. The values determined as shown in *Table* 1 are reasonable compared with the supplier's values.

The pigment was a Co substituted Ba-ferrite magnetic particle (diameter ~ 50 nm, SSA ~ 32 m^2/g). Cyclohexanone and methylethylketone (2:1 mixture) were used as solvents.

Polymer Adsorption

The adsorption amount of the polymer onto the pigment from the solution was determined by the difference in the polymer concentration in the solution before and after the adsorption. In a normal adsorption experiment, the initial concentration of the polymer solution was 0.1 - 2 wt%, and the weight ratio of the pigment and the solution was 1:20. After shaking the mixture for 1.5 hr, the suspension was held at 25°C for 24 hr to allow the pigment to settle. The concentration of the supernatant was then measured.

A sequential adsorption is a continuous adsorption sequence to fractionate the chains. A detailed procedure has been reported elsewhere.[11] In short, the normal adsorption process is repeated by using a new pigment and the retrieved supernatant solution. At each adsorption step, the chains adsorbed onto the pigment are removed from the system. Because the chains having a strong affinity to the pigment preferentially adsorb, the polymer is fractionated by the adsorption strength. The weight ratio of the pigment and the solution was kept at 1:20 for each step.

Paint Dispersion and Evaluation

The model magnetic paints consisting of the Ba-ferrite pigment and the dispersant polymers were prepared by sand milling. For the initial formulation, a pigment-binder ratio was 10/1 and the solid content (SC) was 55 wt%. After four hours of dispersion using a paint shaker, the paste was diluted with the solvent to SC = 35 wt% and dispersed for 30 min. The paint was then coated on a polyethylene terephthalate film and dried. The dispersion of the paint was evaluated by measuring the gloss of the coating film with a haze-glossmeter (BYK-Gardner 4601) at 60° incident angle.

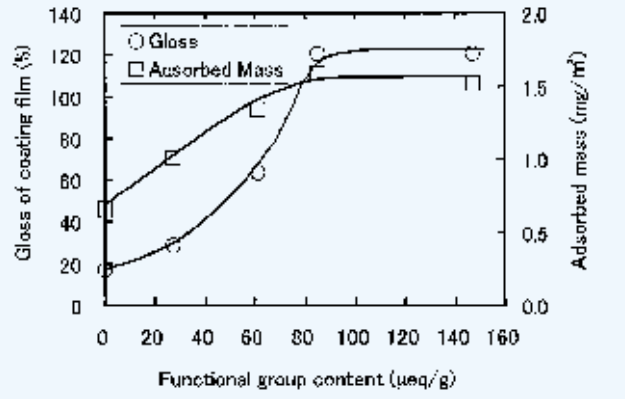

Figure 1—Dispersion and adsorption properties of RSO_3^- functionalized polyurethanes.

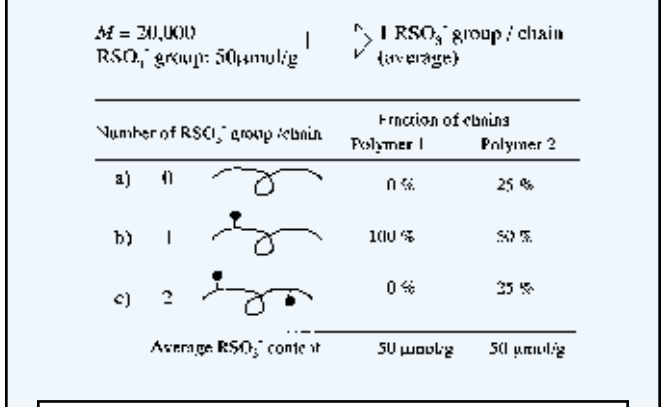

Figure 2—Schematic description of the polydispersity of functional group distribution among the chains.

RESULTS AND DISCUSSION

Effect of the Functional Group

Figure 1 shows the effect of the sulfonate anions on the adsorbed mass and the dispersion quality. With an increase in the RSO_3^- group content in the polymer, both the adsorbed mass and the film gloss increased, and almost saturated beyond 85 m mol/g. The difference in the properties between the nonfunctionalized binder and adequately functionalized ones is significant. These results basically coincide with previous studies showing the effect of functionalized polymers.[5,6]

Functional Group Distribution Among the Chains

Polyester-polyurethane polymers are formed by connecting the polyester chains via urethane units. To simplify the analysis, the following assumptions were adopted in this study. The molecular weight of the polyester unit is 1000, and the urethane unit is ignored (included in the polyester). Hence, in the case of M = 20,000, a polyurethane chain consists of 20 polyester units. The molecular weight of the RSO_3^- functionalized polyester is assumed to also be 1000. The number of RSO_3^- groups on one polyurethane chain is determined by how many functionalized polyesters the chain has. If M = 20,000, the maximum number is 20 and the minimum is zero.

In the case of Polymer B, the experimentally determined RSO_3^- content is 27 m mol/g. This value corresponds to about 0.5 RSO_3^- groups per one polyurethane chain of molecular weight 20,000. As symbolically shown in the decimal value of the content, the number of RSO_3^- groups on the chains is not expected to be homogeneous among the chains. *Figure* 2 shows a schematic image of the functional group distribution. In the case of the 50 m mol/g RSO_3^- content, one of the 20 polyester units is RSO_3^- functionalized. Hence, the polyurethane chain of M = 20,000 (consisting of 20 polyester units) can have one RSO_3^- group on it (type b in *Figure* 2). In an ideally distributed case, all chains take this configuration and there are no nonfunctionalized chains (Polymer 1). However, as a result of the random polymerization, all chains cannot be the same. Typically, there will also exist chains having no RSO_3^- group (type a in *Figure* 2) and chains having two RSO_3^- groups (type c in *Figure* 2). If the ratio of these three cases is 1:2:1 (Polymer 2), the average RSO_3^- content equals 50 m mol/g, but this polymer contains 25% nonfunctionalized chains. Because of this polydispersity, the functional group distribution among the chains underlying the average number is an important factor. In actuality, the distribution is much wider, because the polymer will contain chains having more than two RSO_3^- groups. In addition, a distribution of molecular weight surely exists, which increases the functional group distribution.

The effect of the functional group distribution was evaluated by a model dispersion experiment at the beginning. Sample polymers were mixed to adjust the RSO_3^- content and then used as the binder for the dispersion. For example, Polymer B and Polymer E were mixed at 1:1 to make a binder with an 87 m mol/g RSO_3^- content. These mixed binders are listed in *Table* 2. If the content of the RSO_3^- group dominates the dispersion properties, the mixed binders and the original polymers will show a similar dispersion level at a comparable RSO_3^- content. The dispersion result of the mixed binders is shown in *Figure* 3 together with the results of the original polymers. It is apparent that the content is not enough to explain the dispersion behavior, and the mixed binders show a lower performance. This is supposed to come from the difference in the functional group distribution among the chains. In the case of the 1:1 mixture of Polymer A and Polymer E (Binder F), the average RSO_3^- content of the binder is 74 m mol/g. However, it contains at least 50 wt% nonfunctionalized chains originating from Polymer A, and these chains do not contribute to the dispersion. If the ratio of the functionalized chains in Polymer C (61 m mol/g RSO_3^- content) is higher than 50%, Polymer C has more effective chains and will show a good dispersion performance. This can explain the higher dispersion of Polymer C (film gloss = 63%) than that of mixed Binder F (film gloss = 29%). From the statistical estimation, the functionalized chains in Polymer C is 60 wt% (see *Figure* 4). Also, the experimental results (*Tables* 3 and 4) showed the existence of about 50 wt% functionalized chains in Polymer C. In other words, Polymer C contains 40-50 wt% nonfunctionalized chains in it. Hence, the distribution of the functional group among the chains should be recognized for the precise characterization of the dispersion behavior. Further analysis about the distribution and its effect on the dispersion is discussed in the following sections.

Table 2—Binder Polymers Prepared by the Mixture

Binder	Source 1	Source 2	Ratio (wt)	RSO_3^- (m eq/g)
F	Polymer A	Polymer E	1:1	74
G	Polymer B	Polymer E	1:1	87
H	Polymer A	Polymer E	1:3	110

Statistical Calculation

The functional group distribution of a dispersant polymer can be calculated based on the random distribution of both the molecular weight and the functional

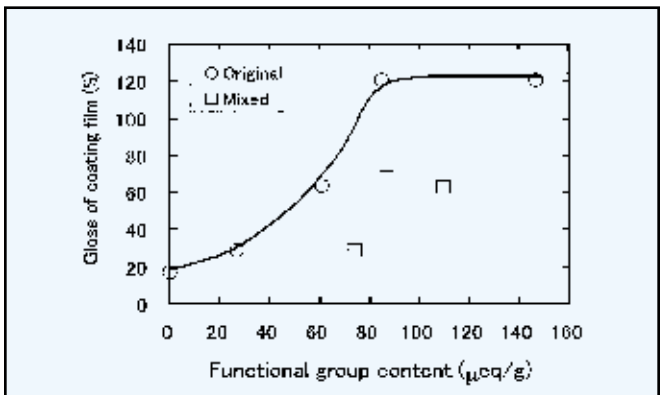

Figure 3—Dispersibility of various RSO_3^- content binder polymers.

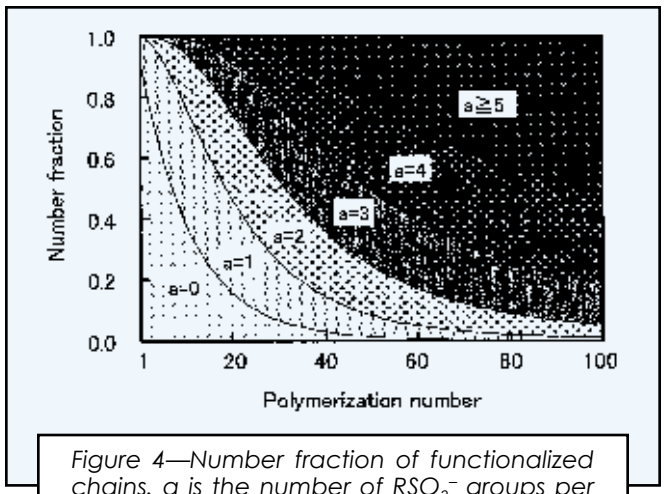

Figure 4—Number fraction of functionalized chains. a is the number of RSO_3^- groups per one polyurethane chain. q is fixed at 0.085.

group. Based on the assumptions discussed in the previous section, the functional group distribution of the polyurethane dispersant polymers was estimated as follows. The functional group content of the polyurethane is controlled by the mixing rate of the functionalized polyesters in the normal ones. When the RSO_3^- content of the polyurethane is s m mol/g, the ratio of the functionalized polyesters (M = 1,000) and nonfunctionalized ones (M = 1,000, one functional group per one chain) is roughly expressed as s:(1000-s). The probability (q) for each polyester chain to be functionalized is expressed by $s/1000$. In the case of the 100 m mol/g RSO_3^- content, the ratio of the functionalized and nonfunctionalized polyesters is 1:9 and one of 10 polyester chains has an RSO_3^- group. When one polyester chain is randomly picked up, the probability that the chain is functionalized is q = 0.1.

Assuming an independent and random distribution of the functionalized polyester chains in the polyurethane chains, the binomial distribution formula can be used to express the functional group distribution. At a fixed polymerization number (x) of polyurethane, the number fraction of the polyurethane chains having a specific number of RSO_3^- groups is expressed by,

$$Pa(x) = \frac{x!}{a!\,x(x-a)!} x(1-q)^{x-a} x q^a, \qquad (1)$$

where a is the number of RSO_3^- functionalized polyesters in one polyurethane chain. In the case of x = 20 and q = 0.1, where the molecular weight of the polyurethane is 20,000 and the probability of encountering the functionalized polyester is 0.1, the number fraction of the nonfunctionalized polyurethane chains (a = 0) is calculated to be P_0 (20) = 0.12. The number fraction of the chains having one functional group (P_1 (20)) or more cases (a > 1) can be calculated in the same manner. In the following calculation, the molecular weight was included up to 100,000 (x = 100), and the number of RSO_3^- groups on the chain was allowed change up to nine.

Figure 4 shows the number fraction of the polyurethane chains in the case of s = 85 m mol/g (q = 0.085). At this RSO_3^- content (same as Polymer D), 41% of the polyurethane chains are nonfunctionalized for a polymerization number of 10 (x = 10), and 17% are still nonfunctionalized at x = 20. Because of the polydispersity of the molecular weight, Polymer D ($M_w \sim 2 \times 10^4$ and $M_w/M_n \sim 2$) contains many chains of polymerization number 10-20. Based on these facts, the existence of nonfunctionalized chains is expected in Polymer D, though it shows good dispersion properties. Another important point is that the chains functionalized with more than four RSO_3^- groups occupy 8% at x = 20. These highly functionalized chains increase to 32% at x = 40. The solubility of these chains is supposed to be poor, and it is not desirable to have many of them. Reducing the nonfunctionalized chains by simply increasing the degree of polymerization will introduce a different problem related to the dispersion process.

For actual polymers, the molecular weight distribution should also be included. For the molecular weight distribution of randomly polymerized polymers, the weight fraction ($F_w(x)$) is calculated using the following formula.[7]

$$F_w(x) = x\, p^{x-1}(1-p)^2, \qquad (2)$$

where x is the polymerization number, and p is the extent of the reaction. At p = 0.905, the average molecular weight calculated from this distribution becomes 20,100 and matches the supplier's values. To evaluate the functional group distribution of polydisperse dispersant polymers, the weight fraction of the chains of specific molecular weight is calculated using equation (2) at the beginning. By using equation (1), the fraction is then divided into subfractions having a specific number of RSO_3^- groups on one chain. By summing up the subfraction over a whole molecular weight region, the weight fraction of the polymer chains having a specific number of RSO_3^- groups is determined.

The result of the p = 0.905 case is shown in *Figure* 5 as a function of the RSO_3^-content of the polymer. When the RSO_3^-content is zero (Polymer A), all chains do not have an RSO_3^- group and the fraction of the a = 0 case is 100%. At a 27 m mol/g RSO_3^- content (Polymer B), 65 wt% of the polymer does not have a functional group. These chains will not

Table 3—Polymer Amount in the Solution During the Sequential Adsorption

Polymer	Initial (g)	1st Step (g)	2nd Step (g)	3rd Step (g)	4th Step (g)
B	1.00	0.83	0.69	0.62	0.56
C	1.00	0.80	0.63	0.55	0.49
D	1.00	0.77	0.57	0.48	0.37
E	1.00	0.76	0.53	0.41	0.34

Table 4—RSO_3^- Amount in the Solution During the Sequential Adsorption

Polymer	Initial (m mol)	1st Step (m mol)	2nd Step (m mol)	3rd Step (m mol)	4th Step (m mol)
B	27	4	0	0	0
C	61	20	4	0	0
D	85	35	17	2	0
E	147	59	22	4	1

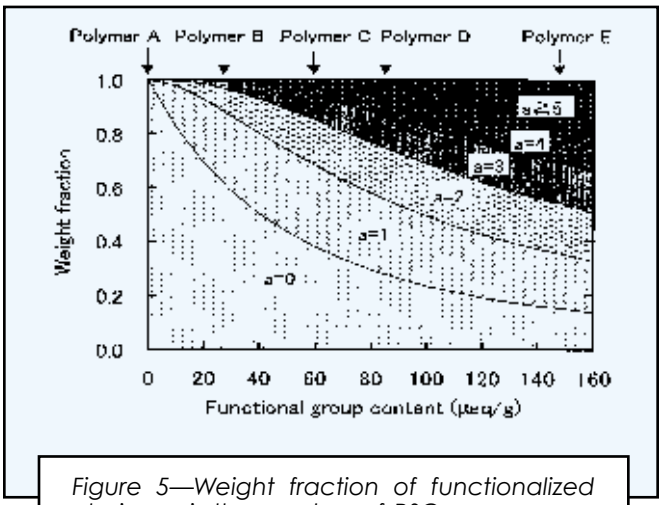

Figure 5—Weight fraction of functionalized chains. a is the number of RSO_3^- groups per one polymer chain. M_w of polyurethane is 2 x10^4 and M of polyester unit is 1000.

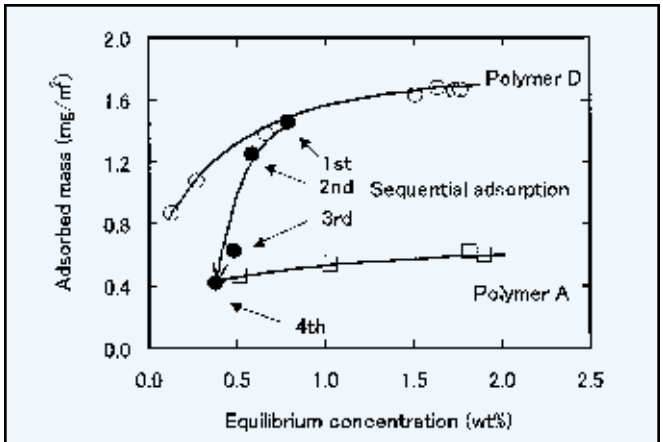

Figure 6—Sequential adsorption of functionalized polymer. Open circles: normal adsorption isotherms, filled circles: sequential adsorption.

contribute to the paint dispersion, and this can explain a lower gloss of the coating film using Polymer B. Even for Polymer E (147 m mol/g), 15 wt% of the polymer are nonfunctionalized chains. At this higher functional group content, highly functionalized chains ($a \geq 4$) occupy more than 30 wt%.

Sequential Adsorption Experiment

The functional group distribution of sample polymers was evaluated by a sequential adsorption experiment. The result for Polymer D is shown in *Figure* 6 with the adsorbed mass isotherms of Polymers A and D. The first adsorption step of the sequential adsorption is the same as a normal adsorption, and the measured adsorbed mass is within the isotherm of Polymer D. At the second step, the supernatant of the first adsorption and the new pigment are used for the adsorption, and the adsorbed mass is lower than the isotherm. This is because a part of the highly functionalized chains, which has a strong affinity to the pigment, is removed from the solution during the first adsorption. At the third step, the difference from the isotherm becomes greater. After the fourth and final step, the adsorbed mass decreases to the same level as the one for the nonfunctionalized binder (Polymer A).

The results of the sequential adsorption for the sample polymers are shown in *Figure* 7. Higher RSO_3^- content polymers keep a higher adsorbed mass for more steps, while the adsorbed mass of the lower RSO_3^- content polymers significantly decreases at earlier steps. This will come from the amount of the RSO_3^- functionalized chains in the polymers. In each adsorption step, 10-25 wt% of the chains are removed from the solution. For the lower RSO_3^- content polymers, all the RSO_3^- functionalized chains are removed during the first and second steps, and the adsorption of the residual chains becomes weaker. Higher RSO_3^- content polymers have enough RSO_3^- functionalized chains to last for the third and fourth adsorption steps, and keep a higher adsorbed mass even in these steps. At the later adsorption steps, the adsorbed mass of four polymers comes close to 15-20 mg/m^2, which is comparable to the adsorbed mass of the nonfunctionalized polymer (Polymer A). After several steps, most of the RSO_3^- functionalized chains are removed from the solution. Hence, the rest of the chains in the solutions are almost nonfunctionalized ones, and the adsorption behavior comes close to that of Polymer A.

Tables 3 and 4 show the results of the fractionation by the sequential adsorption. The values are normalized, as the initial polymer amounts are equal to 1 g. Focusing on Polymer D (85 m eq/g), 0.77 g of the polymer containing 35 m eq of the RSO_3^- group remains in the solution after the first adsorption step. The amount of the adsorbed polymer is 0.23 g, containing 50 m eq of the RSO_3^- group, which means that the RSO_3^- content of the adsorbed polymer is 217 m eq/g. Therefore, highly functionalized chains actually exist and preferentially adsorb. On the other hand, the RSO_3^- amount in the solution becomes zero after the fourth adsorption. All chains having RSO_3^- groups have adsorbed onto the

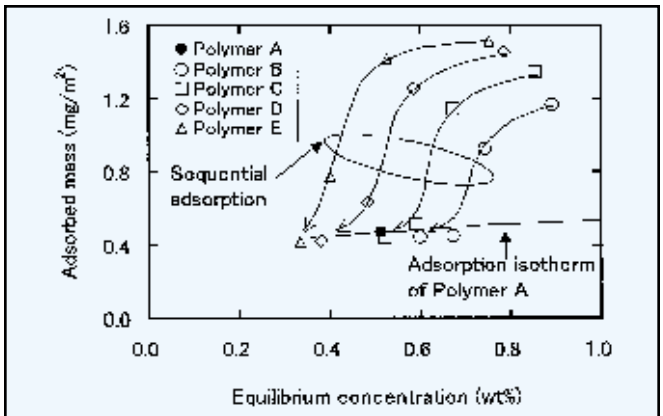

Figure 7—Results of sequential adsorption (open symbols). Steps are proceeding from higher to lower concentration. Adsorption isotherm of Polymer A by normal adsorption is superimposed.

Table 5—Amount of Nonfunctionalized Chains in Functionalized Binders

Binder (Polymer)	RSO_3^- Content (μ eq/g)	Ratio of Nonfunctionalized Chains Calculated (wt%)	Measured (wt%)
A	0	100	—
B	24	65	>69
C	57	40	>55
D	85	28	>37
E	148	15	(<34)
F	74	58	—
G	86	40	—
H	111	37	—

pigment and were removed from the solution. However, the solution still contains 0.37 g of the polymer. It is apparent that these remaining chains do not have RSO_3^- groups on them. Therefore, nonfunctionalized chains also exist and they occupy more than 37 wt%. The same analysis was done for the other polymers, and a minimum weight of the nonfunctionalized chains is estimated in *Table* 5 together with the result from the calculation. The matching of the results is not perfect, but the trend is reasonable. The experimental error will increase for the later adsorption steps because of the lower RSO_3^- content and accumulated weight loss. A calculation error will come from the assumptions used. The distributions will not perfectly obey the formulas. The average molecular weight and other parameters are not strictly precise. Some of the chains included in the calculation may not be practical based on the solubility and the actual polymerization process. Considering these factors, the results will be acceptable as a first approximation.

The dispersion result shown in *Figure* 3 was adjusted to account for the actual amount of functionalized chains (using calculated values). *Figure* 8 shows the gloss of the films versus the ratio of the functionalized chains in the polymer. Because the binder amount is fixed in the formulation, the ratio corresponds to the actual weight of the functionalized chains in the paint. These results show a better consistency than does *Figure* 3. Because the functionalized chain is so effective in improving the dispersion, the dispersion properties of dispersant polymers are more precisely described by the exact amount of the functionalized chains.

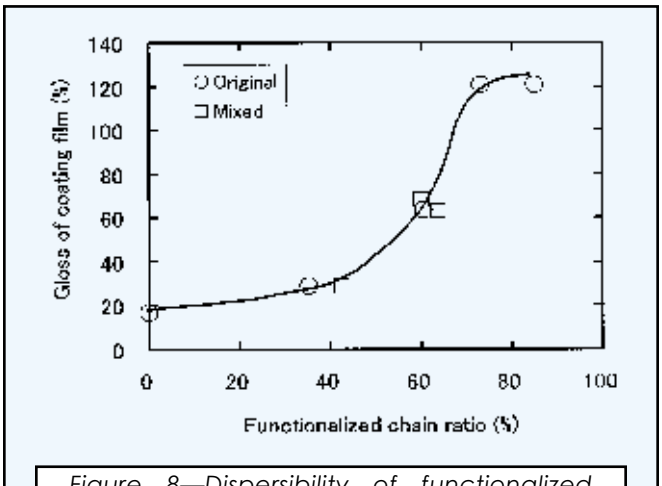

Figure 8—Dispersibility of functionalized binder polymers arranged by the ratio of actual functionalized chains (calculated).

CONCLUSIONS

Industrial-grade polydisperse dispersant polymers contain both a molecular weight distribution and a functional group distribution. The existence of nonfunctionalized chains and overfunctionalized ones caused by the distributions is not a negligible factor. For example, by statistical calculation, the RSO_3^- functionalized polyurethane dispersant polymers ($M_w \sim 2 \times 10^4$) were found to contain 65 wt% nonfunctionalized chains at 25 μ mol/g RSO_3^- content, and 15 wt% even at 148 μ mol/g. Sequential adsorption experiments proved the existence of both overfunctionalized and nonfunctionalized chains. The amount of nonfunctionalized chains in the polymers determined by the experiments roughly matched the calculated results. The dispersion behavior was better clearly explained by considering the actual amount of the functionalized chains in the paints.

Recognizing the existence of the different level of functionalized chains in a random polymerization polymer will help to more efficiently design paint formulations and powder dispersions. It might also be added that there is considerable discussion in the literature regarding the effect of one or more functionalized chains in thermosetting resin systems prepared by random copolymerization. The analysis described in this paper may be of significant value in understanding these systems and various other applications using functionalized polymers.

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