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Abstract

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STUDY OF GRAFT COPOLYMERIZATION OF VINYL CHLORIDE WITH DERIVATIVES OF THE METHACRYLIC SERIES

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When a monomer is polymerized in the presence of polymeric substances, the latter are acted upon by radicals of the growing chains or of the initiator. In this case, as a result of chain transfer, active centers may arise on the macromolecules, capable of initiating polymerization of the monomer with the formation of high-molecular compounds of branched or three-dimensional structure. If the chemical nature of the side branches and of the main chain is different, graft copolymers are formed, combining the properties of the polymers taken into the reaction.

The synthesis of graft copolymers through the interaction of polymers with monomers was developed and acquired technical significance in 1946–1947 ([1,2]). In later works, methods of graft copolymerization are described that are based on the use of ionizing radiation and on the interaction of functional groups of macromolecules with monomeric or polymeric substances ([3–6]).

Below are given experimental data on the synthesis and study of graft copolymers obtained by polymerization of vinyl chloride in a latex of a copolymer of butyl methacrylate and methacrylic acid (BMA), as well as graft copolymers formed during polymerization of a mixture of butyl methacrylate and methacrylic acid in a polyvinyl chloride (PVC) latex.

Table 1

Polymer	Cl, %	$[\eta]$	K'	f
Grafted VC on BMA (1 : 2)	21,7	0,820	0,441	0,668
Control PVC	56,0	0,402	0,331	–
Control BMA-5	–	0,90	0,159	–
Mechanical mixture PVC + BMA-5 (1 : 2)	18,8	0,69	0,165	–

The polymerization of vinyl chloride in BMA latex was carried out in an autoclave in the presence of ammonium persulfate at a temperature of 45–60° and

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

at various ratios of the reagents. CCl_4 and CHJ_3 were used as regulators. The copolymers obtained were reprecipitated three times with methyl alcohol from a solution in cyclohexanone, extracted with acetone to free them from unreacted BMA, and dried to constant weight. In the copolymers, bound chlorine, the degree of interaction of the monomer with the polymer f, the characteristic viscosity, and the Huggins constant K' were determined. To prove the formation of a graft copolymer, turbidimetric titration (7) of its solution was carried out.

Analogous determinations were made for BMA, PVC, and the mechanical mixture of these polymers.

As is seen from Table 1, the Huggins constants of the graft copolymers are higher than those of the control linear polymers, which indicates branching that has arisen owing to the formation of side chains. The Huggins constants

the intrinsic viscosity of PVC mixtures with BMK lie between the values of the constants for the individual polymers and are quantities close to additive ones.

The coefficient of interaction of the monomer with the polymer, f, shows that more than 60% of the monomer enters into reaction with the polymer.

For turbidimetric titration, solutions of the polymers in dioxane or in a mixture of dimethylformamide with acetone ($C = 0.005\%$) were placed in a T-shaped cuvette and titrated with a mixture of isopropyl alcohol—water (3 : 1) or methanol—water (19 : 1), with automatic delivery of the precipitant at a constant rate of 3.33 ml/min. To measure turbidity, the optical system of an FNK-51 nephelometer and an EPP-09 recording potentiometer were used.

Fig. 1. Turbidimetric titration of polymer solutions in a mixture of dimethylformamide and acetone with methyl alcohol containing 5% water:
1 –graft copolymer of vinyl chloride (38.4%) on BMK-5 (61.6%);
2 –mechanical mixture of PVC (33.2%) + BMK-5 (66.8%).

Fig. 2. Thermomechanical properties of the graft copolymer BMK–PVC in comparison with a mixture of polymers and individual ingredients of the mixture.
1 –copolymer of BMK (95 wt. parts) and methacrylic acid (5 wt. parts),
2 –polyvinyl chloride (PVC),
3 –mixture BMK + PVC (1 : 1),
4 –graft copolymer BMK–PVC (1 : 1).

As can be seen from Fig. 1, when titrating the mixture of polymers, separate precipitation is observed, whereas the precipitation curve of the sample obtained by polymerization of vinyl chloride in BMK latex indicates the presence of a graft copolymer.

A study of the influence of the monomer—polymer ratio, the polymerization regulator, and temperature on the yield and properties of the graft copolymers showed that increasing the amount of vinyl chloride in the mixture of components leads to an increase in the utilization coefficient f and in the yield of graft copolymer (see Table 2).

Table 2

Initial ratio VC : BMK by weight	Analysis of copolymers before extraction: Cl, %	Analysis of copolymers before extraction: η_{ud}	Analysis of copolymers after extraction: copolym., %	Analysis of copolymers after extraction: Cl, %	Analysis of copolymers after extraction: η_{ud}	Analysis of copolymers after extraction: f	Analysis of copolymers after extraction: T_g	Analysis of copolymers after extraction: T_f
1 : 1	23.4	0.70	71.0	26.2	1.16	0.650	50	190
2 : 1	34.5	0.57	74.1	35.3	0.92	0.705	75	170
4 : 1	39.8	0.63	82.0	41.2	0.67	0.753	80	155
1 : 1*	23.9	0.45	52.8	28.4	–	0.455	58	160
4 : 1*	44.8	0.31	46.7	48.7	0.37	0.315	63	140
PVC	56.0	0.25	–	–	–	–	70	140
BMK	–	0.40	–	–	–	–	40	–
PVC + BMK**	27.5	0.40	55.9	46.5	0.43	–	57	135

* Obtained in the presence of CCl_4 (10 wt. % of the monomer).
** Mechanical mixture PVC + BMK-5 = 1 : 1.

The addition of a regulator (CCl_4, CHI_3) sharply reduces the yield of graft copolymer, evidently by inactivating part of the macroradicals.

Studies of thermomechanical properties on V. A. Kargin' s apparatus show that graft copolymers, in contrast to mixtures of homopolymers of the same composition, pass into the viscous-flow state at a considerably higher temperature ($T_f = 190$ instead of 135°) and differ little in the value of T_g (see Fig. 2).

Changing the ratio VC : BMA in the graft copolymer from 1 : 1 to 4 : 1 sharply raises T_g (from 50 to 80°) and lowers T_f (from 190 to 155°).

Along with the study of graft copolymers with a BMA backbone and PVC side chains, copolymers with the reverse order of grafting were synthesized.

Fig. 3 and Fig. 4 graphs

Figure 2: Fig. 3 and Fig. 4 graphs

For this purpose, a mixture of butyl methacrylate (95 parts by weight) and methacrylic acid (5 parts by weight) was added to a polyvinyl chloride latex; the PVC : BMA ratio was 1.12. After four hours of emulsification of the monomers in the PVC latex at 60°, an initiator $(0.5\%(\mathrm{NH}_4)_2\mathrm{S}_2\mathrm{O}_8)$ was introduced and polymerization was carried out to practically complete conversion of the monomers. The product obtained was purified and studied in the same way as the graft copolymers BMA–PVC.

In the case of grafting BMA onto PVC, the content of bound chlorine increases by a factor of 7-8 in the fraction passing into solution during 50-hour extraction with acetone or with the azeotropic mixture chloroform (47%)–acetone (30%)–methanol (23%).

Fig. 3. Turbidimetric titration of polymer solutions in dioxane with a mixture of isopropyl alcohol and water.
1 –graft copolymer PVC–BMA, 2 –PVC, 3 –graft copolymer BMA–PVC, 4 –BMA

Fig. 4. Thermomechanical properties of graft copolymers of BMA and PVC with the direct and reverse order of grafting.
1 –grafting BMA onto PVC (1 : 1), 2 –grafting PVC onto BMA (1 : 1)

This increase in solubility is apparently due to the formation, on the macromolecules of the low-molecular-weight PVC fraction, of more readily solvated BMA side chains.

Figure 3 gives the titration curves of solutions of the “direct” (BMA–PVC) and “reverse” (PVC–BMA) graft copolymers.

The points of incipient precipitation of the “direct” and “reverse” graft copolymers are very close and lie between the points of incipient precipitation of the homopolymers.

Figure 4 indicates a sharp difference in the thermomechanical properties of copolymers with the direct and reverse order of grafting at practically the same component ratio and value of f. When BMA is grafted onto PVC, products are obtained with a higher T_g and a lower T_f than in the case of the reverse order of grafting. Thus, comparison of the data on the thermomechanical properties of “direct” and “reverse” graft copolymers leads

to the conclusion that, other conditions being equal, the nature of the main chain has the strongest effect on the glass-transition temperature, whereas the side branches, which form the spatial structure, are reflected primarily in the temperature interval of viscous flow.

An increase in the length of the side chains intensifies their effect on the T_g of the copolymer (see Table 2), since in this case the flexibility of the main chain depends to a greater extent on the flexibility and intermolecular interaction of the side branches.

It should also be noted that the character of the thermomechanical curves of the graft copolymers differs from analogous curves for mixtures of homopolymers by the presence of two plateaus (cf. the curves in Figs. 2 and 4).

The graft copolymers BMK–PVC are of considerable practical interest, since they combine the high adhesion and light resistance characteristic of BMK with the increased resistance to abrasion, water, benzene, and oils, the chemical resistance, and the nonflammability of polyvinyl chloride.

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REFERENCES CITED

1. A. A. Berlin, Author' s Certificate 70763, class 39B, 402, 11 X 1946; Author' s Certificate 73031, class 39 4202, 19 X 1946; Author' s Certificate 68062, 15 IV 1946, 39 4202; Author' s Certificate 77731, 39, 23 XI 1948.
2. R. Compragnon, J. Le Bras, *Rev. Gen. Cautch.*, **24**, 4 (1947); French Patent No. 972455 (1951).
3. A. A. Berlin, T. A. Makarova, *ZhOKh*, **21**, 138 (1951).
4. A. A. Berlin, Collection, *Successes in Polymer Chemistry*, 1957, p. 13.
5. M. S. Akutin, *Khim. nauka i prom.*, **2**, 5, 585 (1957).
6. P. P. Radchenko, *Kauchuk i rezina*, **16**, 7, 13 (1957).
7. J. Henstenberg, *Zs. Electrochem.*, **60**, No. 3, 236 (1956).
8. H. W. Melville, *Polym. Sci.*, **16**, 505 (1955).

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