On the Graft Polymerization of Styrene and Acrylonitrile onto Polybutadiene in the Presence of Vinyl Acetate. I. Preparation of Graft Polymers

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SYNOPSIS

In order to modify the graft polymers of styrene and acrylonitrile onto polybutadiene (ABS polymers), the preparation of the graft products of styrene, acrylonitrile, and vinyl acetate onto polybutadiene rubber by emulsion polymerization was described and theoretically studied up to a high degree of conversion. Depending on the residual monomer content of the products, the polymer composition obtained in the experiment was compared with the theoretical one for the substitution of certain quantities of styrene, acrylonitrile, or styrene and acrylonitrile by vinyl acetate in the mass ratio of 3 : 1. Deviations were discussed. The specific viscosity of the polymers of styrene, acrylonitrile, and vinyl acetate separated from the elastomer phase, considerably decreases during the substitution of acrylonitrile by increased vinyl acetate quantities.

INTRODUCTION

Since the introduction of the graft products of styrene and acrylonitrile onto polybutadiene (ABS) in the early fifties, their manufacture and application have been followed worldwide by a large variety of applications.[1] These polymers can be also matched to specific fields of application by modifying both the elastomer and rigid phase. So, the use of polyacrylate or EPDM rubber results in polymers with a higher resistance of the elastomer phase, e.g., to the UV and thermal-oxidative influence. The modification of the rigid phase, e.g., by addition of methyl methacrylate, gives transparent molding materials while the heat distortion temperature may improve by adding α-methyl styrene or maleimides.[2]

In the following, the manufacture of the graft products of styrene and acrylonitrile onto polybutadiene that were formed by substituting part of the monomers by vinyl acetate will be described. Another paper[3] will deal with the studies of the properties of these polymers that show improved physical and technical characteristics under certain conditions[4] as well as their behavior when blended with other components.

THEORETICAL FUNDAMENTALS

The graft polymerization of styrene, acrylonitrile, and vinyl acetate onto polybutadiene rubber is a very complicated problem and is considered to be in the first approximation a terpolymerization of monomers with respect to the composition of the graft products. Since, after sifting, the two-parameter model proved also to be applicable to the copolymerization of styrene and acrylonitrile as well as of styrene and vinyl acetate,[5] the equation established by Alfrey and Goldfinger for the description of the correlation between monomer and polymer composition[6] is suggested to be valid for the respective terpolymerization. Whenever available, the copolymerization parameters calculated and verified by Kelen and Tüdös[5] and being equal to those of the mass polymerization have been selected for the subsequent calculations (see Table I).

After testing the ternary azeotropy according to the criteria of Tarasov[10] and Valvassori and Sartori,[11] no such point was shown for the styrene–

Table I   Selected Copolymerization Parameters for the Styrene–Acrylonitrile–Vinyl Acetate System

| Monomer 1	Monomer 2	r_{12}	r_{21}	T (K)	Reference
Styrene	Acrylonitrile	0.41	0.07	343	7
Styrene	Vinyl acetate	61	0.056	343	8
Acrylonitrile	Vinyl acetate	4.05	0.061	333	9

acrylonitrile–vinyl acetate system in accordance with Arita et al.[7] For the only binary azeotrope, 61.2 mol % of styrene and 38.8 mol % of acrylonitrile were calculated.

To study the terpolymerization behavior at different conversion degrees, the Alfrey–Goldfinger equation has been integrated and solved by a computer program according to the Runge–Kutta principle in equidistant conversion steps of 1 mol %.

Figure 1 indicates the computed dependence of the terpolymer composition on the composition of the monomer mixture at low conversion degrees (2 mol %) for the styrene–acrylonitrile–vinyl acetate system. As can be seen, vinyl acetate can be incorporated in the polymer only to a small extent. This quantity increases with rising vinyl acetate amount in the monomer mixture while the amount of styrene

or acrylonitrile is kept constant. At the same time the difference between the monomer mixture and polymer composition becomes larger.

At higher conversion degrees, the behavior of the terpolymerization system varies as shown in the result of calculations. If the composition of styrene and acrylonitrile in the monomer mixture is azeotropic, styrene–acrylonitrile copolymers with constant composition are formed. They contain only a small acetate quantity, which after the styrene and acrylonitrile monomers have been consumed at higher conversion degrees turns relatively rapidly into nearly pure vinyl acetate homopolymers. In case of deviations from the styrene–acrylonitrile azeotrope toward a higher styrene content in the monomer mixture, styrene–acrylonitrile copolymers of variable composition with a low vinyl acetate con-
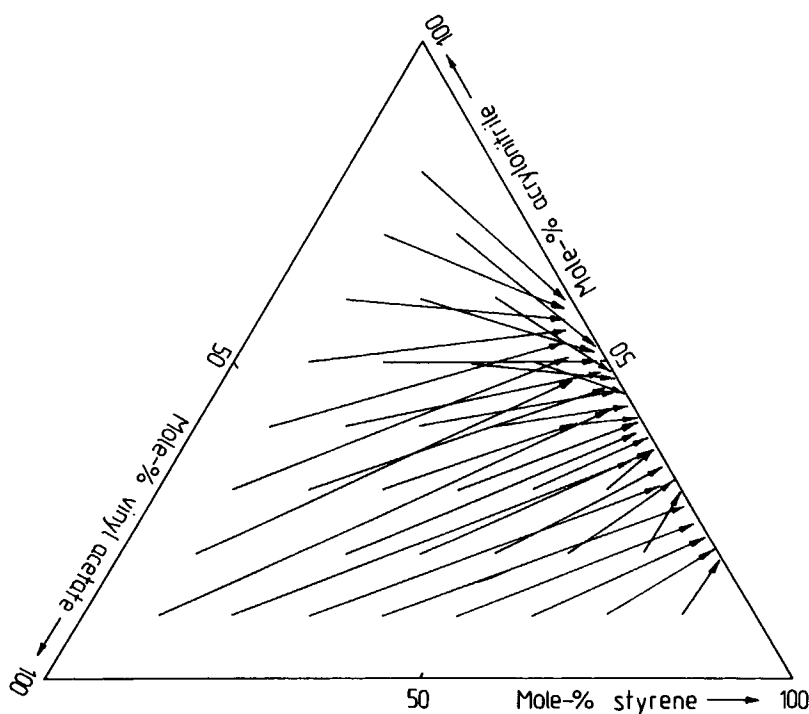
Figure 1   Dependence of the terpolymer composition on the composition of the monomer mixture for the styrene–acrylonitrile–vinyl acetate system.
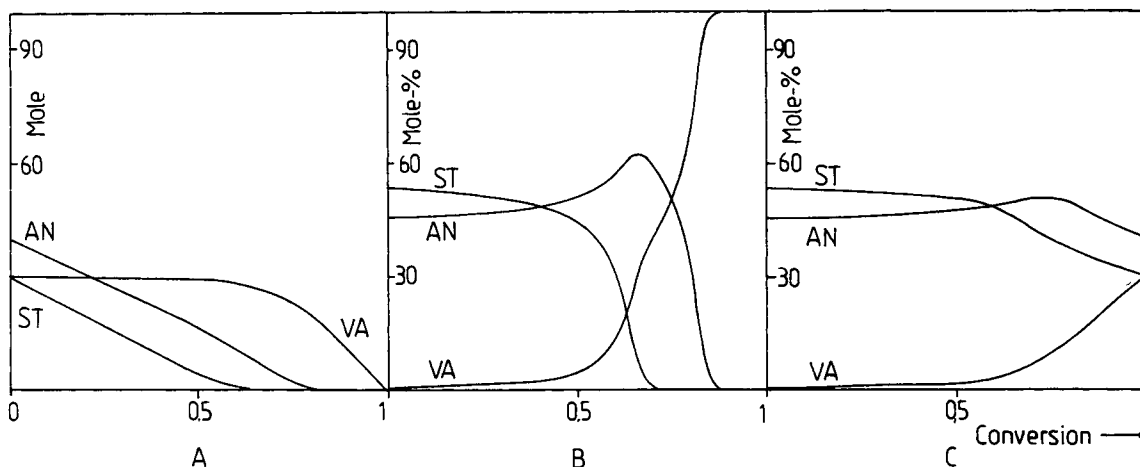
Figure 2 Dependence of the (a) monomer composition, (b) differential, and (c) integral terpolymer composition on the conversion for the styrene (ST, 30 mol %), acrylonitrile (AN, 40 mol %), and vinyl acetate (VA, 30 mol %) system.

tent are formed at a low degree of conversion and mainly vinyl acetate homopolymers at a high degree of conversion.

Deviations from the styrene–acrylonitrile azeotrope toward a higher acrylonitrile content in the monomer mixture (Fig. 2), also cause styrene–acrylonitrile copolymers of variable composition with a low vinyl acetate content at a low degree of conversion. After the styrene is consumed, the styrene–acrylonitrile copolymers change into acrylonitrile–vinyl acetate copolymers of greatly variable composition. After consumption of acrylonitrile they change mainly into vinyl acetate homopolymers. The acrylonitrile maximum in the differential terpolymer composition [Fig. 2(b)], e.g., at constant acrylonitrile concentration (40 mol %), shifts toward lower conversion degrees with rising vinyl acetate quantity in the monomer mixture (for 5 mol % of vinyl acetate, maximum at 94 mol % of conversion degree; for 15 mol % of vinyl acetate, maximum at 84 mol % of conversion degree; for 30 mol % of vinyl acetate, maximum at 66 mol % of conversion degree).

EXPERIMENTAL

The graft products were formed in emulsion polymerization using the following basic formulation:

Rubber content: 18.5% wt
Ratio of the organic to the aqueous phase: 1 : 2
E 30 emulsifier (from VEB LeunaWerke): 2% wt (as related to the monomers)

Tert. dodecyl mercaptan: 0.6% wt (as related to the monomers)
$K_2S_2O_8$: 2 × 0.1% wt (as related to the monomers)
Mass ratio of styrene to acrylonitrile: 3 : 1

When using vinyl acetate, a certain quantity of monomers was substituted by vinyl acetate. As a graft basis, an emulsion polybutadiene latex with a number-average particle size of 54 nm and a 1,4-*cis* content of 15%, a 1,2 content of 18%, and a 1,4-*trans* content of 67% in rubber was used.

Having charged the feedstocks, the graft polymerization was initiated by heating the autoclave at a constant heating circuit temperature of 363 K. When after about one hour the peak temperature was exceeded and the temperature of the circuit reached again, the second charge of $K_2S_2O_8$ was fed for repeated initiation. For another hour, the polymerization was performed at 363 K without the use of pressure. In the end, the ABS latex formed was precipitated by a magnesium chloride solution to obtain the polymer. It was washed several times, stabilized by 0.5% 2,6-di-*tert*-butyl-*p*-cresol and 0.7% trisnonylphenyl phosphite and oven-dried at 333 K to constant weight.

The composition of the graft products was determined by elementary analysis of the nitrogen content or oxygen content under consideration of a blank reading.
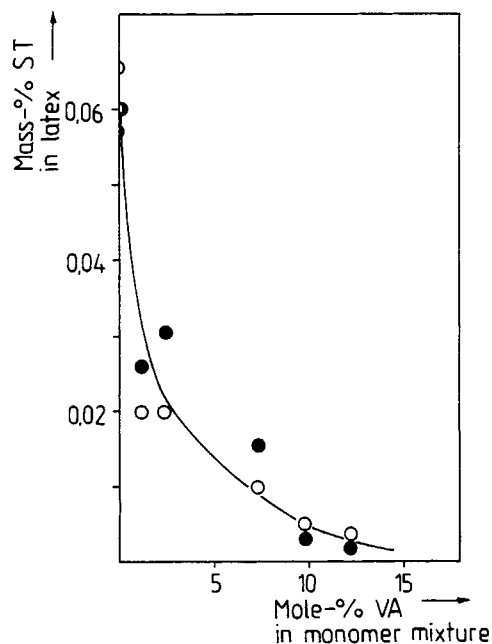
The ungrafted polymers of styrene, acrylonitrile, and vinyl acetate were separated from the elastomer phase grafted to some extent, by extraction of the precipitated ABS by acetone. The specific viscosity of the polymers from styrene, acrylonitrile, and vinyl

acetate, which had been separated by acetone extraction and precipitation by ethanol, was determined on a 0.5% solution in dimethyl formamide by means of the Ubbelohde viscosimeter.
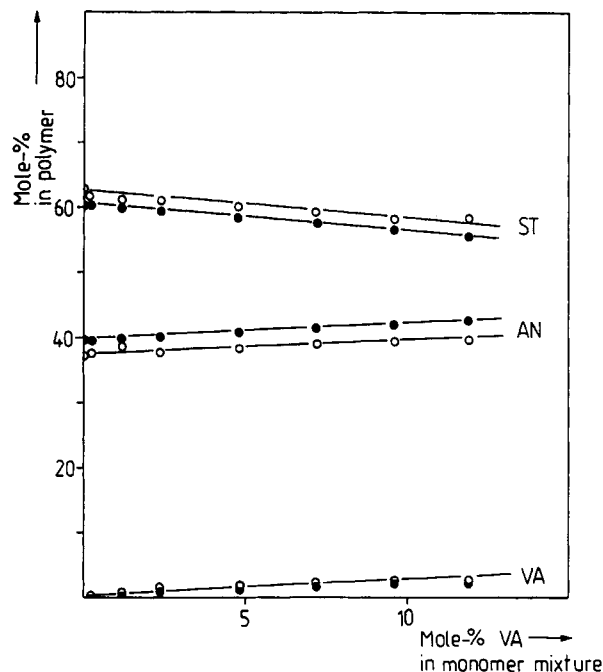
RESULTS AND DISCUSSION

For the preparation of ABS polymers the emulsion polymerization was found to be suitable. This type of polymerization was performed up to a high polymerization conversion. Based on the theoretical studies already discussed, styrene, acrylonitrile, or both monomers were substituted nearly to their azeotrope (the mass ratio of styrene to acrylonitrile being 3 : 1) by increasing quantities of vinyl acetate.

The influence of the vinyl acetate content in the monomer mixture on the residual styrene contained in the ABS latex as an important characteristic of this latex is shown in Figure 3 for the styrene substitution. In the experiment a considerable decrease of the residual styrene quantity has been observed with rising vinyl acetate content. This has been confirmed by the two analytical methods applied (direct gas chromatographic analysis of the styrene content in the ABS latex and steam distillation of

Figure 4   Change of the polymer composition related to styrene (ST), acrylonitrile (AN), and vinyl acetate (VA) with rising quantity of vinyl acetate in the monomer mixture for styrene substitution: (O) experimental; (●) theoretical.

Figure 3   Dependence of the residual styrene content in the ABS latex on the vinyl acetate quantity in the monomer mixture for the substitution of styrene by vinyl acetate: (O) analysis of the ABS latex by GC; (●) steam distillation of the ABS latex and analysis of the organic phase by GC.

the ABS latex followed by gas chromatographic analysis of the composition of the organic phase).[12] Figures 4 to 6 indicate the composition of the graft polymers formed by emulsion polymerization, as related to the monomers styrene, acrylonitrile, and vinyl acetate as a function of the vinyl acetate quantity used for the styrene substitution, acrylonitrile substitution and styrene–acrylonitrile substitution. For comparison, the compositions as calculated earlier and related to the corresponding experimental residual styrene content as the degree of conversion are shown.

As can be seen from the figures, in qualitative accordance with theory, the acrylonitrile content in the polymer increases with rising vinyl acetate quantity in the monomer mixture and in the polymer in case of styrene substitution whereas the styrene content decreases. In case of acrylonitrile substitution, the acrylonitrile quantity in the polymer decreases considerably while the styrene content clearly increases. The substitution of styrene and acrylonitrile in a nearly azeotropic ratio results only in a slight decrease of the styrene and acrylonitrile quantity in the polymer.

Moreover the figures show that the vinyl acetate content in the polymer is in good agreement with
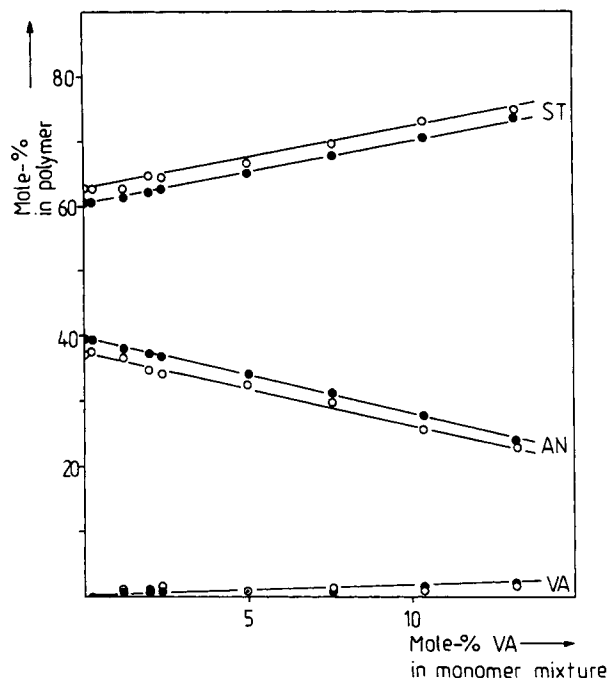
Figure 5 Change of the polymer composition related to styrene (ST), acrylonitrile (AN), and vinyl acetate (VA) with rising quantity of vinyl acetate in the monomer mixture for acrylonitrile substitution: (○) experimental; (●) theoretical.
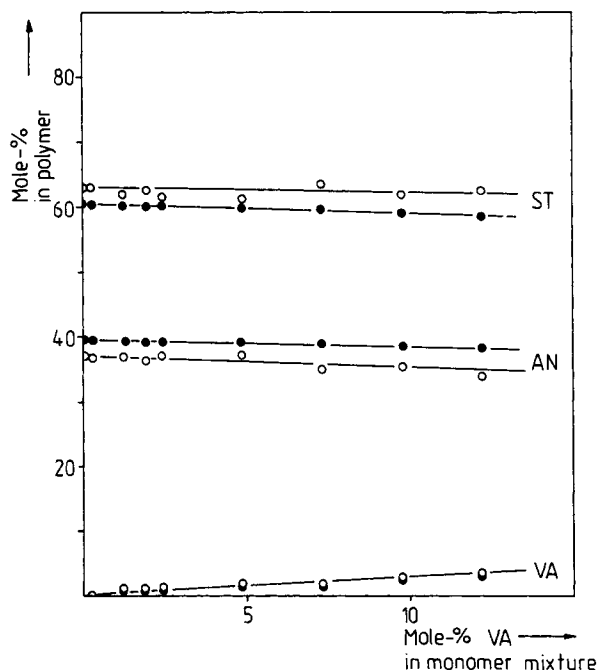
Figure 6 Change of the polymer composition related to styrene (ST), acrylonitrile (AN), and vinyl acetate (VA) with rising quantity of vinyl acetate in the monomer mixture for the substitution of styrene and acrylonitrile in the mass ratio 3 : 1: (○) experimental; (●) theoretical.

the theoretical value for the respective conversion. However, the styrene content in the polymer is found to be always higher and the acrylonitrile content in the polymer lower by about 2 to 4 mol % each when compared with the theoretical values. The most significant reason lies obviously in the different solubility of the monomers in the aqueous and organic phase as shown earlier for the emulsion polymerizations of styrene and acrylonitrile,[13,14] and styrene, acrylonitrile, and methyl acrylate.[15,16] Acrylonitrile of 7.35% wt has a relatively good water solubility at 293 K[17] while that of vinyl acetate of 2.0–2.4% wt is relatively low at 293 K[18] and that of styrene of 0.032% wt at 298 K[19] is negligible. The solubilities mentioned vary highly by addition of emulsifiers.[20] Other reasons being related to the deviations from the validity of the Alfrey–Goldfinger terpolymerization equation are less probable.

The various monomer solubilities or monomer contents in the aqueous phase, in the monomer droplets, or in the swollen polymer particles as the reaction location proper may be considered at constant polymerization temperature for the styrene–acrylonitrile system by introducing the parameter

$$B = \frac{S_{mp}}{A_{mp}}$$

where S_{mp} is the styrene concentration in the polymer particles and A_{mp} is the acrylonitrile concentration in the polymer particles in the Mayo–Lewis equation. In particular, this parameter is a function of the distribution coefficient of acrylonitrile and the monomer–water ratio.[21] Within the conversion range of 80–100% the styrene content in the copolymer has been found to be higher by 7 to 0 mol %. This styrene content is in good agreement with the experimental results. The data obtained above for the styrene–acrylonitrile–vinyl acetate system are also within this range.
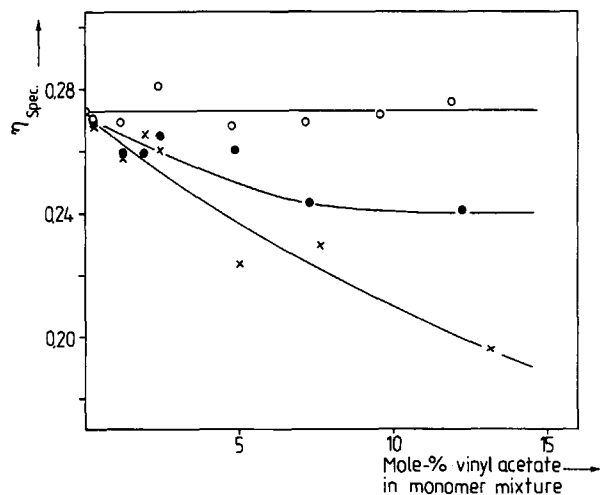
Further it is to be considered that when using the styrene–acrylonitrile–vinyl acetate system, a graft polymerization onto a polybutadiene rubber takes place.[22] As visible from Table II the degree of swell-

Table II Degree of Swelling of Pure Polybutadiene in Different Monomers at 296 K

Monomer	Degree of Swelling
Styrene	6.30
Acrylonitrile	1.10
Vinyl acetate	1.68

ing of pure polybutadiene in the monomers (as the quotient of the masses of the test piece swollen for 48 h at 296 K and the one unswollen) greatly differs. It is mainly the diffusion of styrene that takes place. If the polybutadiene is swollen and grafted by the monomer mixture, then this might result in an inner grafted content in the rubber particles that has a higher styrene content and a lower acrylonitrile content compared to the other polymers formed in the system. Thus, the inner grafted content is similar to the effect caused by the monomer solubilities.

The dependence of the specific viscosity of the polymers from styrene, acrylonitrile, and vinyl acetate, separated from the elastomer phase, on the vinyl acetate quantity used for the monomer mixture is plotted in Figure 7 for the substitution of styrene, of acrylonitrile, as well as of styrene and acrylonitrile in the mass ratio of 3 : 1. While the specific viscosity of the separated polymers does not vary considerably in the styrene substitution with increasing vinyl acetate quantity in the monomer mixture, it decreases in the substitution of styrene and acrylonitrile and particularly clearly in the substitution of acrylonitrile. This should be related to the differentiated chain transfer behavior of vinyl acetate in relation to the comonomers. The viscosity data obtained are attributable to a noticeable decrease of the molecular weights of SAN copolymers and in case of graft po-

lymerization of styrene and acrylonitrile onto polybutadiene rubber according to Ref. 23, clearly change the physical properties.

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Figure 7 Change of the specific viscosity of the polymers separated from the elastomer phase and obtained from styrene, acrylonitrile, and vinyl acetate with rising amount of vinyl acetate in the monomer mixture: (O) styrene substitution; (X) acrylonitrile substitution; (●) substitution of styrene and acrylonitrile in the mass ratio of 3 : 1.