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Copolymerization of Styrene and Acrylonitrile in the Presence of Ethylene-Propylene Copolymer

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Dedicated to Prof. Dr. Hermann Mark on the occasion of his 85th birthday

SUMMARY

The degree of conversion, intrinsic viscosity, composition and particle average size distribution of styrene (S)- acrylonitrile (AN) copolymer, formed mainly under heterogeneous conditions and in the presence of EPM, were investigated as function of the reaction time. An induction period, characterized by unstable preferential solvatation phenomena, is followed by a regular copolymerization period which can be described by apparent S and AN reactivity ratios. The regular copolymerization at high conversion is ascribed to the formation of EPM-g-SAN which acts as an emulsifier in the reaction system.

INTRODUCTION

A large number of papers dealing with the influence of the medium on the copolymerization of styrene (S) and acrylonitrile (AN) has been published. The interest stems from the deviation of the reactivity ratio values obtained for heterogeneous copolymerizations (MINO, PEEBLES, ODIAN et al.) from those concerning bulk, emulsion and homogeneous copolymerizations which yield similar values (LEWIS et al., FORDYCE and CHAPIN, RUDIN and KRUSE). Different hypotheses were put forward in the past to account for the discrepancies observed, but a satisfactory explanation of the complex picture of experimental data so far collected is lacking.

Several years ago, MINO and PEEBLES proposed that preferential adsorption of the monomers onto the copolymer surface could explain the composition difference between SAN synthesized in solution and under heterogeneous conditions.

More recently, RIESS and DESVALOIS explained some compositional anomalies observed when SAN is grafted onto polybutadiene or ethylene-propylene based terpolymers (EPDM) by means of preferential solvation phenomena. PICHOT et al. demonstrated through differential refractometry and dialysis equilibrium of ternary systems (solvent-monomer-polymer) that different concentrations of monomer actually exist in proximity of polymers present in homogeneous media and the monomer distribution strictly depends on the composition of the system considered.

We have investigated the copolymerization of S and AN and attempted to determine their reactivity ratios when SAN is formed in presence of EPM (ethylene-propylene copolymer), i.e. when also EPM-g-SAN is formed (CESCA et al.). Since the graft efficiency is low (i.e. < 10%) under the conditions adopted, it is possible to separate ungrafted SAN from EPM-g-SAN and ungrafted EPM and to analyze isolated SAN.

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EXPERIMENTAL

Materials, procedure and analyses were described previously by ARRIGHETTI et al. and CESCA et al. The AN content of SAN was determined by nitrogen analysis (micro Dumas method; Perkin Elmer mod. 240 instrument). The results were the average of at least two determinations. The error was ± 0,3% of the nitrogen content of samples. Morphological investigations were carried out with transmission electron microscopy (Siemens Elmiscope 2A instrument) on samples taken from the polymerization suspension and diluted with solvent (isooctane).
A computer program (IBM 4331) was used for calculating the copolymer composition according to the integrated Skeist equation (CHAN and MEYER).

RESULTS AND DISCUSSION

Copolymerization

Typical conversion-time plots of S-AN copolymerization, giving both free and graft copolymer, are shown in Fig. 1.
Icreasing amounts of AN in the feed influence markedly the copolymerization process by enhancing the overall polymerization rate and favouring the precipitation of SAN.
The formation of EPM-g-SAN since the early stage of reaction prevents SAN clogging, observable when S-AN copolymerization is carried out without EPM in aliphatic hydrocarbons, because graft copolymers act as oils in oils emulsifiers within systems formed by incompatible polymers (MOLAU, RIESS et al.). Actually, SAN separation takes place uniformly as a finely divided powder (s. below) which appears emulsified by other components of the reaction system (suspension-emulsion). The induction time, occurring during the first 5-15 minutes of reaction, corresponds to the intermediate period between the solution and the suspension-emulsion state of the reaction mixture.
This time is shortened by increasing the AN concentration of the feed. The separation of SAN involves a decreased diffusion of the chain propagating free radicals and hence termination processes become less important (PEEBLES). Consequently, the overall copolymerization rate increases (Tromsdorff effect) and the intrinsic viscosity of SAN increases sharply during the induction time (Fig. 2). Interestingly, when SAN copolymerization is carried out in a homogeneous medium (s. lower diagram of Fig. 2), the intrinsic viscosity of the copolymer is constant during the reaction time investigated.
The content of AN in SAN formed at different degrees of conversion and with different feed composition, is shown in Fig. 3. A sharp modification of the copolymer composition is evident for each feed composition during the induction period, the extention of which decreases when the AN content increases. Moreover, the amount of AN in the copolymer produced at low conversion is significantly lower than that predicted by the homogeneous copolymerization data (LEWIS et al.). Apparently, steady state conditions are reached after the induction time since the curves of Fig. 3 follow the expected trend of classical radical copolymerization (s. below). The small size of SAN particles (s. the next section) and the emulsion-like character of the reaction medium, accounts for the inexistence of mass transfer phenomena, also at high conversion.
When the copolymerization solvent is changed (Fig. 4), the trend of the composition vs. the monomer conversion results rather similar to that of Fig. 3 in the case of n-heptane

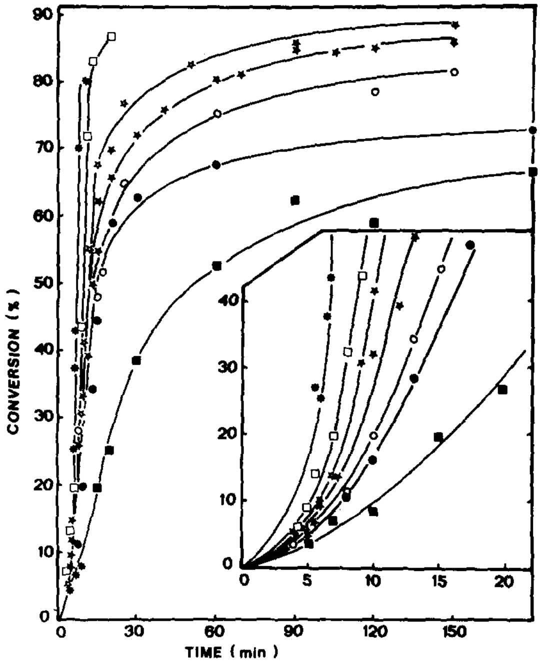


FIG. I: Time course of S-AN conversion in the presence of EPM (42.0 g/l; C_2H_4= 71 mole %; [η]=1.98 dl/g in toluene, 30°C). Conditions: 90°C; Isooctane; initiator = t-butyl-5-ethyl-perhexanoate (4.6 mmole/l); S+AN= =1.95 mole/l; AN/(AN+S):(■)=25.0, (●)=39.5,(○)=48.0, (★)=53.0,(☆)=56.7, (□)=66.2,(✱)=79.9 mole %.

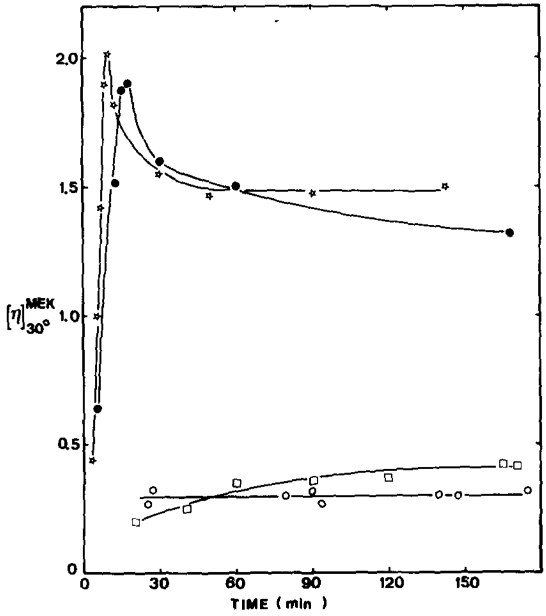


FIG. 2: Dependence of the intrinsic viscosity of SAN on the copolymerization time. Conditions and symbols as in Fig. 1, except: (□)=n-heptane+toluene (1:1 by vol.), (○)=toluene. Other conditions for the lower diagrams: 83°C;benzoyl peroxide=4.95 mmole/l; S+AN=2.55 mole/l, mole ratio = =1.54; EPM=20.6 g/l.

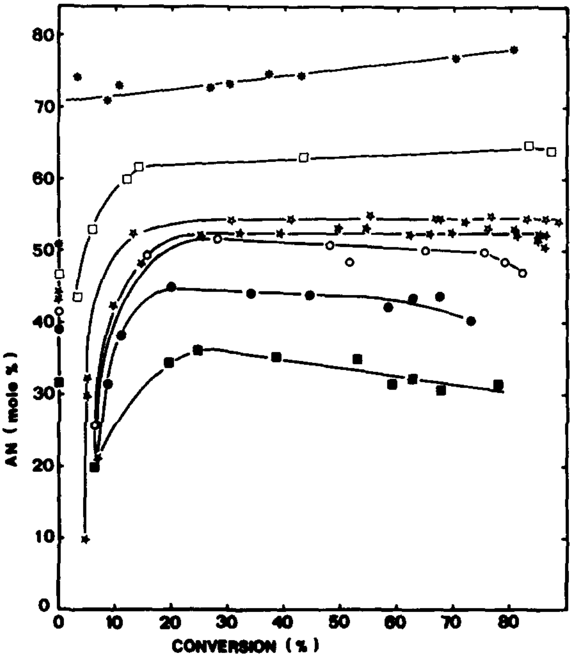
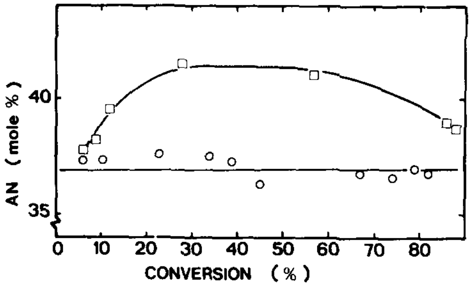


FIG. 3: SAN composition vs. conversion at different feeds. Conditions and symbols as in Fig. 1. The values calculated according to LEWIS et al. are shown on the ordinate.

FIG. 4: SAN composition vs. conversion. Samples obtained in toluene(○) and n-heptane+toluene (1:1 by vol.) mixture. Conditions as in Fig.2 (lower diagrams).



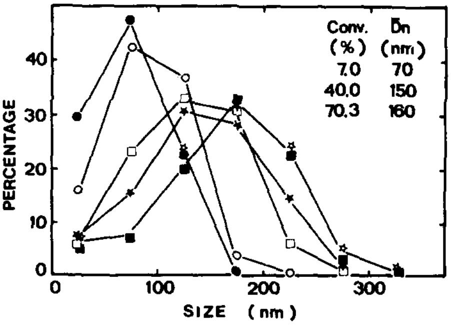


FIG. 5: Particle size distribution of SAN obtained at different conversions. Conditions as in Fig.1; AN in the feed = = 53.5 mole %. Conversion:(●)=7, (○)=13,(□)=27,(★)=40,(■)=64,(☆)=70%. D_n = number average diameter.

-toluene mixture (unable to dissolve SAN).

Conversely, the composition of SAN remains almost constant within a broad range of conversions when solvent (e.g. toluene) is able to dissolve SAN, even though the azeotropic composition predicted by LEWIS et al. was approximated but not reached.

The last findings suggest that preferential solvation effects, which occur not only under heterogeneous conditions (PEEBLES, RIESS and DESVALOIS) but also in homogeneous media (PICHOT et al.), are of scarce importance when SAN is formed in toluene under the conditions adopted. As the copolymer composition is independent of the conversion degree, the formation of SAN occurs on active centers which may be trapped by EPM or SAN chains, but possible gradients of monomer concentration have low values. Conversely, when the copolymerization takes place in an aliphatic hydrocarbon which dissolves EPM and S, but poorly AN, a preferential solvation of EPM by S seems to occur initially. This hypothesis appears likely if one bears in mind the solubility parameters of n-heptane, EPM, S and AN which are (at 25°C) 7.4, 7.9, 8.6 and 10.4 $(cal/cm^3)^{0.5}$, respectively. Actually, the composition of initial SAN is extraordinarily rich in S, at least for feed compositions up to 66 mole % of AN. The introduction of AN into the chains of SAN increases the solvation of the copolymer by AN (the solubility parameter of SAN can be calculated as 9.8 $(cal/cm^3)^{0.5}$ for the azeotropic composition), whose concentration augments progressively when the conversion increases. Therefore, great part of the copolymerization process occurs onto separated copolymer where the relative concentration of the monomers is different from the initial one and from that existing in solution.

The linear part of the diagrams of Fig. 3 resembles the plot obtainable from the SKEIST equation which, after integration, has been used to calculate the expected behavior of some copolymerization systems (CHAIN and MEYER). This possibility implies, in our case, the assumption that the copolymerization of S and AN in the presence of EPM reaches a "steady state" after the induction period. This assumption may be accounted for by the formation of a sufficient amount of a dispersing agent, i.e. EPM-g-SAN, which stabilizes a system that is intrinsically heterogeneous.

The stabilization effect concerns with the adsorption by SAN of S and AN whose relative concentrations are substracted to the variations induced by preferential solvation effects which are due to the fast change of the copolymer composition during the induction period.

Therefore, the copolymerization of S and AN at high conversion and in the presence of a dispersing agent should be described by the classical copolymerization equation. This fact appears possible since Fig. 3 shows that an "azeotropic" composition exists at ca. 55 mole %. Moreover, feeds containing amounts of AN lower than the "azeotropic" composition give SAN which is progressively poorer in AN and viceversa, when the feed is richer in AN.

Morphology

In order to gain more insight of the SAN separation process, a morphological investigation of the suspended particles formed in isooctane was carried out by transmission electron microscopy. The change of the diameter of the particles formed with "azeotropic" composition (AN = 55 mole %) is shown in Fig. 5 where the size distributions observed at six different conversions are plotted. Changes of both the shape of the distribution curve and the size region occur at conversion $< 15\%$. Non "azeotropic" compositions yield SAN which shows (Fig. 6) the same trend of Fig. 5.

The results obtained indicate that the distribution of the particle diameters observed at low conversions are narrow and situated in the region of lower sizes, i.e. 30-100 nm. The particle number average diameter, calculated from the distribution curves and shown in Figs. 5, 6 is almost independent of the feed composition and suggests the existence of the two distinct reaction periods formerly discussed.

Interestingly, the number average diameter of the particles remains constant ($\bar{D}_n = 160 - 170$ nm) up to high conversions, after the initial period, and this result confirms the stability of the suspension-emulsion formed, independently of the concentration of the monomers and their relative abundance.

Monomers reactivity

Fig. 3 shows that the SAN composition, in particular that of samples containing less than 65 mole % of AN, hardly can be extrapolated to zero conversion. However, this procedure would be meaningless in our case since the initial presence of EPM gives rise to unstable preferential solvation phenomena which influence the composition of SAN formed at low conversion.

Therefore, only the composition data of Fig. 3 subsequent to the induction period can be utilized for calculating apparent reactivity ratios of S and AN formed in the presence of EPM-g-SAN.

By evaluating the feed composition existing at the end of the induction period and the corresponding copolymer composition, it is possible to calculate the values $r_S = 0.342 \pm 0.007$ and $r_{AN} = 0.418 \pm 0.011$ (KELEN and TUDOS; Fig. 7). These values differ from those obtained during the homogeneous copolymerization of S and AN ($r_S = 0.41 \pm 0.08$ and $r_{AN} = 0.04 \pm 0.04$). Consequently, the "azeotropic composition" is observed when the mole fraction of AN is 0.53 instead of 0.38. The separation of SAN, which adsorbs preferentially AN, accounts for the higher value of r_{AN} observed under heterogeneous conditions.

The plot of the SAN composition vs. the monomer conversion, according to the Skeist equation, fits fairly well the experimental data (Fig. 8), corrected for the contribution of the copolymer formed during the induction period, and obtained up to 85% of conversion.

This result has practical relevance since the graft copolymerization of SAN onto EPM yields ABS-like materials displaying interesting technological properties (CESCA et al.).

In conclusion, despite the existence of complex preferential solvation and adsorption phenomena during the S-AN copolymerization in aliphatic hydrocarbons containing dissolved EPM, mass transfer effects play a negligible role so that the SAN composition can be described at high conversion by the classical two-parameter copolymerization equation.

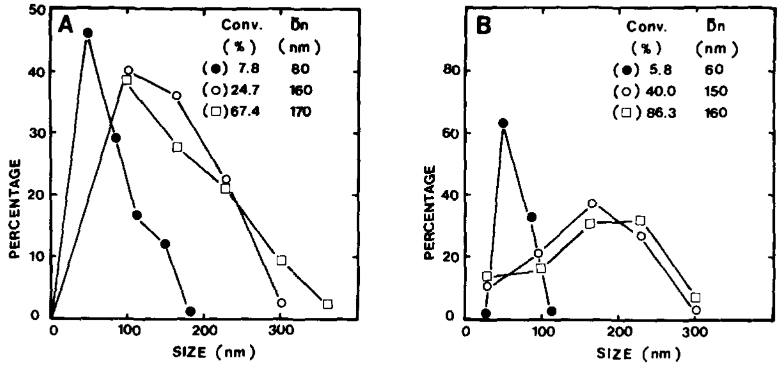


FIG.6: Particle size distribution of SAN produced at different conversions. Conditions as in Fig. 1; AN in the feed: A) 25.0 mole %, B) 66.2 mole %.

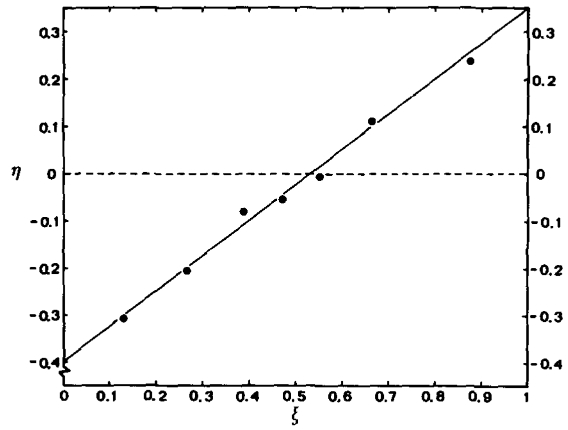
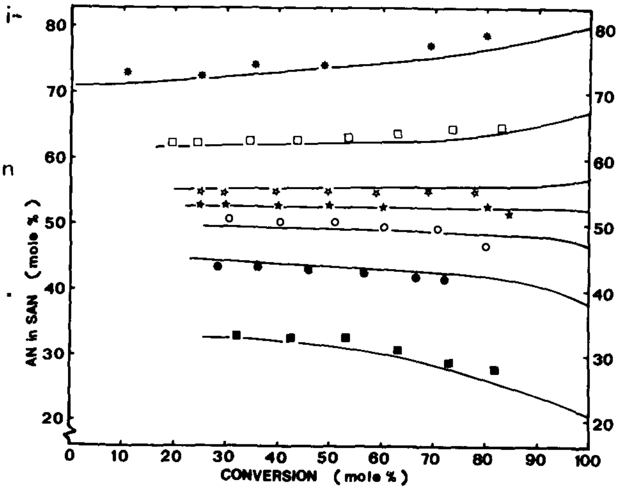


FIG. 7: Evaluation of S and AN "reactivity ratios" according to KELEN and TUDOS (α = 1.053). Experimental data taken from Fig. 3.

FIG.8: Cumulative average SAN composition calculated according to the Skeist equation and using the "reactivity ratios" determined in Fig.7. Experimental points from Fig. 3.



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