G.p.c. and viscometric investigation on grafting of styrene-co-acrylonitrile polymer to ethylene propylene elastomer

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(*Received* 5 *December* 1979; *revised* 9 *September* 1980)

Ethylene-co-propylene polymer (EPM) has been grafted by styrene–acrylonitrile (SAN). The grafting and molecular parameters of the graft polymers (EPM-g-SAN) have been investigated by means of viscometry and g.p.c. measurements. Viscometric molecular weight ($\bar{M}_{v,g}$) parameters of the elastomeric backbone of the graft polymers and distribution of SAN content in relation to grafting conditions have been determined. Viscometric measurements in solvent mixtures have been made on EPM-g-SAN to study the functions of the SAN/EPM ratio and the molecular weight of grafted SAN. Viscometric behaviour is dependent on each of these factors.

INTRODUCTION

This paper is directed to physico-chemical investigations of the radical-induced grafting of styrene–acrylonitrile (SAN) with 75 wt % of styrene onto ethylene-co-propylene polymer (EPM) containing 62 wt % of ethylene. The pure graft polymer, EPM-g-SAN, was isolated by solvent removal of ungrafted SAN and EPM copolymers from the reaction product.

The graft polymer was free from gel and although soluble in only a few liquids some investigations in solution were possible. We have examined the influence of the grafting reaction on molecular weight distribution (*MWD*) of the parent EPM, evaluated some molecular parameters of the graft polymers and investigated their viscometric behaviour in solvent mixtures.

EXPERIMENTAL

Materials

The EPM had an intrinsic viscosity in toluene at 30° of 2.15, corresponding to a viscometric molecular weight of 250000 and a polydispersity index $\bar{M}_w/\bar{M}_n$, of 5.3, as obtained by g.p.c.; it had been prepared according to Cesca[1].

All solvents were chemical grade and used without further purification. Styrene and acrylonitrile were distilled before use.

Preparation of graft polymer[1]

The grafting reaction was carried out at 80°C under an inert atmosphere of nitrogen in a glass reactor equipped with stirrer and thermometer. A known amount of azeotropic styrene–acrylonitrile mixture (76/24 by wt) was added to a known quantity of EPM dissolved in a hydrocarbon solvent (toluene–heptane mixture or isooctane). The reaction started when the predetermined quantity of t-butyl peroctonate had been added and was terminated by addition of a few ml of isopropanol containing 5% of antioxidant (Irganox 1076).

The reaction products were isolated by pouring the reaction suspension into isopropanol, filtered off and dried under vacuum. The resulting material consisted of the graft polymer together with ungrafted SAN and EPM.

Ungrafted SAN was extracted by methyl ethyl ketone and the ungrafted EPM by hexane. The residue after the extractions consisted of graft polymer. The SAN content of graft polymer and the SAN/EPM ratio were determined from the nitrogen content.

Physico-chemical analysis

G.p.c. measurements were carried out with two Waters Associated instruments, GPC Model 200 and ALC/GPC Model 201, using THF as eluant at a flow rate of 1 ml min^{-1}. The GPC Model 200 had a set of four columns packed with Styragel of nominal pore sizes from 5×10^3 to 10^7 Å while the ALC/GPC Model 201 had a set of five columns packed with μ-styragel of nominal pore sizes from 500 to 10^6 Å. The ALC/GPC 201 is also equipped with an ultraviolet (u.v.) detector which coupled to the refractive index (RI) detector enables two chromatograms to be obtained at the same time for EPM-g-SAN. The first chromatogram corresponds to the RI variation for the whole graft polymer and the second one to the u.v. absorption of the SAN grafted onto EPM; both chromatograms are a function of elution volume, V, and molecular weight (see *Figure 4*). Areas of both chromatograms for graft polymers having different SAN contents were measured with a Coradi planimeter to check if there were linear relationships between u.v., RI responses and SAN content. *Table 1* gives experimental values for (a) u.v. absorption specific areas and (A) RI variation specific areas, for some graft polymers. Specific variation areas of RI for SAN and EPM, S and C respectively, and u.v. specific absorption area for SAN, s, have been experimentally determined and reported in *Table 1*.

EPM does not absorb at 254 nm. For evaluating the SAN content distribution in the graft polymers, weight fractions of SAN, X, have been calculated as a function of elution volume by the experimental ratio A/a using the

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Table 1 G.p.c. specific areas for graft polymers with different SAN contents and for EPM and SAN copolymer recorded by u.v. (*a*) and RI (*A*) detectors

Sample	SAN (%)	*a* ($cm^2\ mg^{-1}$)	*A* ($cm^2\ mg^{-1}$)
EPM	0	0	33.1
GP1	17.8	22.8	46.8
2	20.5	18.4	50.7
3	21.4	30.8	52.4
4	23.7	36.0	57.3
5	27.3	37.2	56.5
6	51.0	72.0	82.4
SAN	100	156	122

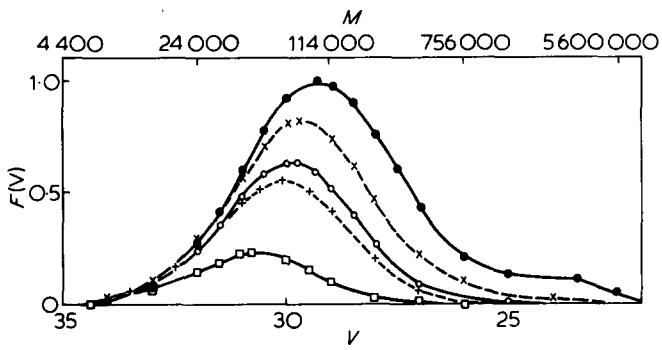

Figure 1 Trend of normalized g.p.c. curves of ungrafted EPM's with respect to parent EPM (●) as a function of weight fraction W_u of ungrafted EPM's (*X*, W_u = 0.8; ○, W_u = 0.6; +, W_u = 0.5; □, W_u = 0.2)

following relationship[2]

$$X = \frac{C/s}{\frac{A}{a} - \frac{S}{s} + \frac{C}{s}},$$

where $C/s = 0.21$ and $S/s = 0.78$.

Viscometric measurements were carried out at 30°C with an Ubbelohde viscometer. Solvent mixtures were prepared by volume at 30°C.

RESULTS AND DISCUSSION

G.p.c. of ungrafted EPMs

The radical induced grafting of SAN onto EPM does not lead to graft polymer only, therefore the physicochemical investigation has been concerned with all the products of the reaction: pure graft polymer, ungrafted SAN and ungrafted EPM. It was observed that the intrinsic viscosities of ungrafted EPM polymers, extracted by hexane from the reaction products, decrease as the quantities of grafted EPM increase. Such a phenomenon is expected on the basis of a statistical interpretation of the grafting reaction even if some degradation should also occur.

Ungrafted EPM samples extracted by hexane from reaction products obtained under different grafting conditions were injected in the GPC Model 200 and the chromatograms were compared with those of parent EPM. *Figure 1* shows elution volume curves of some ungrafted EPMs compared with that of parent copolymer. The area of each chromatogram is proportional to weight fraction, W_u, of ungrafted EPM.

W_u is defined as weight fraction of ungrafted EPM with respect to weight of whole parent copolymer:

$$W_u = \frac{\text{weight of ungrafted EPM}}{\text{weight of whole parent EPM}}$$

All g.p.c. curves of ungrafted EPM shift towards lower molecular weights as fast as W_u decreases but do not cross the elution curves of parent EPM.

These results indicate that grafting reaction occurs preferentially onto the highest molecular weight parent EPM for statistical reasons, without evident degradation. Number average molecular weight and polydispersity indices of ungrafted EPMs, calculated from g.p.c. curves, decrease as W_u does, tending towards as asymptotic value (*Figure 2*). These limit values of $\bar{M}_n/\bar{M}_w$ and $\bar{M}_n$ characterize the fraction of parent EPM which cannot be grafted under our experimental conditions.

Viscometric molecular weight of the backbone for graft EPM, $\bar{M}_{v,g}$

Collins and coworkers[3] have derived an equation to calculate the viscometric average molecular weight of backbone chains in graft polymers using some experimentally accessible quantities: i.e. the molecular weight of the parent polymer, molecular weight of the ungrafted portion, and weight fraction of the original polymer which remains ungrafted.

We have calculated $\bar{M}_{v,g}$ of backbone of graft polymers

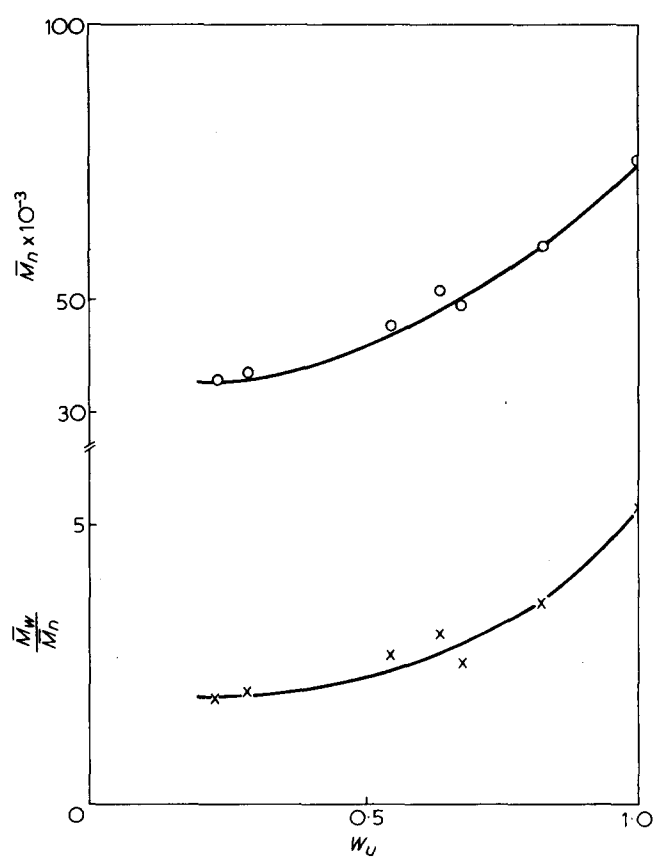

Figure 2 Number average molecular weight, ○, and polydispersity index, *x*, for ungrafted EPM's as a function of W_u

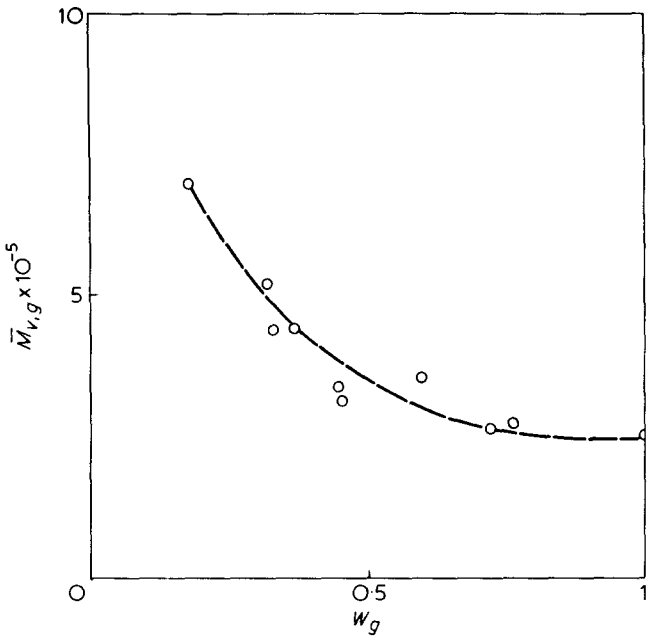

Figure 3 Viscometric average molecular weight of the backbone chain for EPM-g-SAN as a function of weight fraction of grafted EPM

EPM-g-SAN using the following equation

$$\bar{M}_{v,g}=\left(\frac{\bar{M}^a_{v,p}-w_u\bar{M}^a_{v,u}}{1-W_u}\right)^{1/a}$$

and experimental data from intrinsic viscosity and weight fraction measurements.

$\bar{M}_{v,p}$ and $\bar{M}_{v,u}$ are respectively the viscometric average molecular weights of the parent and ungrafted portion of the EPM copolymer, a is the exponent of the Mark–Houwink equation $[\eta]=K\bar{M}^a_w$. For EPM in toluene at 30°C

$$[\eta]=3.1\times10^{-4}\,\bar{M}^{0.72}_w$$

Figure 3 shows the results of applying these equations. $\bar{M}_{v,g}$ of graft polymers decreases as amount, $W_g=1-W_u$, of grafted polymer increases. When the whole parent polymer is grafted, the molecular weight, $\bar{M}_{v,g}$, of graft polymer is equal to that of parent polymer, $\bar{M}_v$, and not less than this value.

These results show that the molecular weight of the backbone chain of a graft polymer depends on the grafting conditions and degradation should not occur during the reaction.

SAN content distribution for EPM-g-SAN

The distribution of grafted SAN onto EPM backbone chains for graft polymers has been determined by evaluating the pairs of g.p.c. curves obtained with the ALC/GPC Model 201 instrument which is equipped with two detectors, one sensitive to the whole graft polymer (RI detector) and the other to the benzene ring of the SAN copolymer (u.v. detector). *Figure 4* shows the chromatograms for three graft polymers having increasing SAN content but different SAN distributions. The abscissa of the *Figure 4* is an increasing function of the molecular weight of the samples.

The areas of the chromatograms obtained under equal experimental conditions increase as the SAN content of samples increases. The first sample of *Figure 4* shows a homogeneous distribution of grafted SAN to the EPM backbone. The two other pairs of chromatograms show different kinds of heterogeneous SAN distributions. The SAN contents as an inverse function of elution volume for the three EPM-g-SAN samples have been derived from the previous pairs of chromatograms and are plotted in *Figure 5*.

The first sample shows a constant SAN content in the whole range of molecular weights.

The second shows a preferential enrichment of grafted SAN at the lowest molecular weights and the third at the highest molecular weights.

SAN content distribution is dependent on the grafting conditions and influences the graft polymer performance. A homogeneous distribution of grafted SAN has usually been observed for graft polymers obtained from toluene/heptane mixtures.

Viscometry of EPM-g-SAN polymer in mixed solvents

Intrinsic viscosity $[\eta]$ of a polymer depends primarily on the ratio $(\bar{R}^2_0)^{3/2}/M$ consisting of a volume divided by

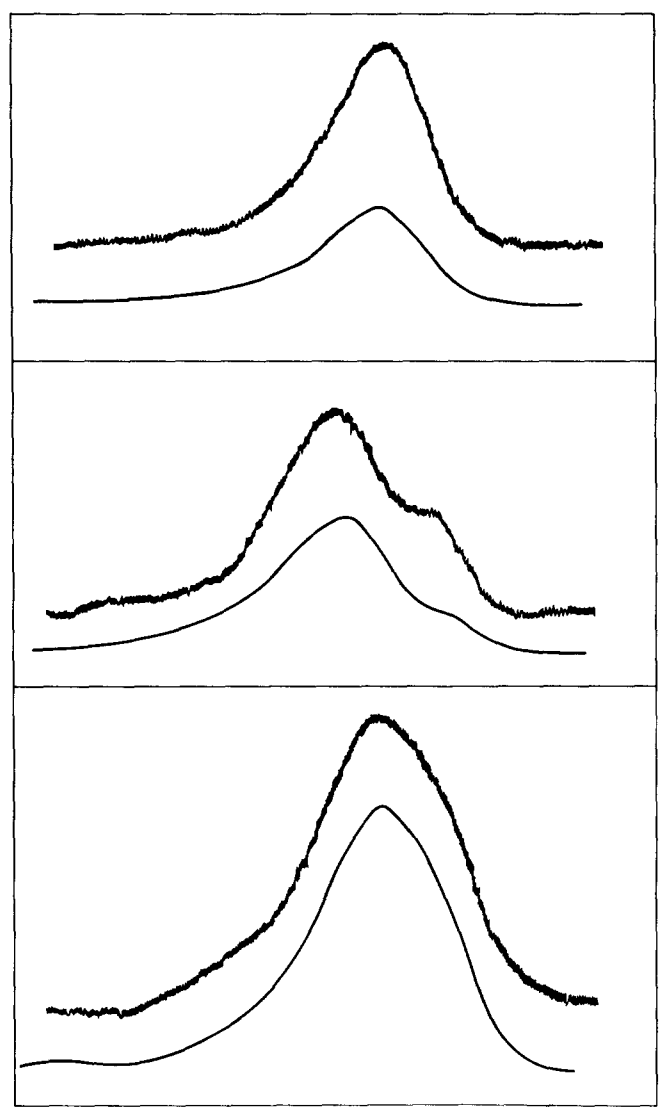

Figure 4 Refractive index (——) and ultraviolet absorption (——) chromatographic traces for three EPM-g-SAN having increasing SAN content and different SAN distribution as an increasing function of molecular weights in abscissa

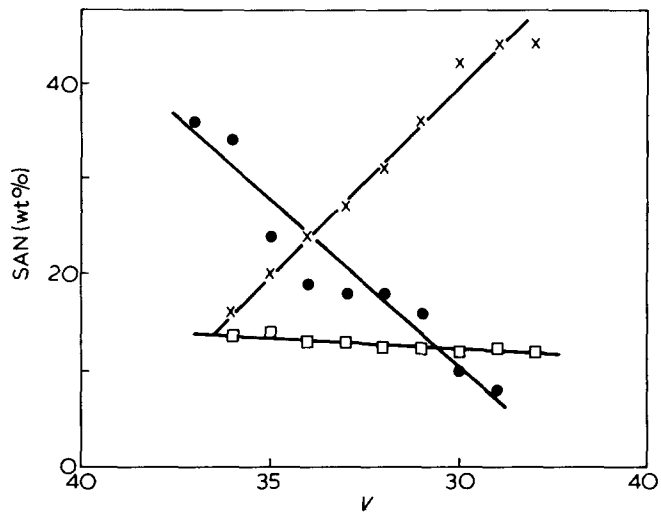

Figure 5 SAN contents as a function of elution volumes for the three above mentioned EPM-g-SAN. Symbols □, ● and X correspond to the first, the second and the third pairs of chromatograms of *Figure 4*

molecular weight and secondly on α^3, the expansion factor related to the solvent:

$$[\eta] = \varphi \frac{(\bar{R}_0^2)^{3/2}}{M} \alpha^3$$

where φ is a hydrodynamic constant and $(\bar{R}_0^2)^{1/2}$ the unperturbed end-to-end distance of the macromolecule.

As a result, for a given polymer of known ratio $(\bar{R}_0^2)^{3/2}/M$ the better the solvent the greater is the expansion factor α^3 of the molecule and the higher the intrinsic viscosity.

When a graft polymer is dissolved in a suitable solvent mixture a preferential solvation by one of the two liquids can occur on the polymer backbone or the grafted branches. Both cases bring about a change of end-to-end dimension of the graft polymer, $(\bar{R}_0^2)^{3/2} \cdot \alpha^3$, and thus a change of $[\eta]$. Viscometric behaviour of graft and block polymers, either as a function of temperature of solvent composition, has been the object of research with information being obtained about polymer conformations. Our graft polymers are insoluble in many of the usual polymer solvents but several are soluble in tetrahydrofuran and chlorobenzene. In order to distinguish the different roles played in solution by the elastomeric backbone and by the SAN grafts, intrinsic viscosity measurements of EPM-g-SAN samples in binary solvent mixtures have been carried out in two series of experiments using mixtures of chlorobenzene and isooctane in the first series and chlorobenzene and methyl ethyl ketone in the second series. Isooctane is a good solvent for EPM and a non-solvent for SAN while MEK is a good solvent for SAN and a non-solvent for EPM. *Figure 6* shows on two cartesian quadrants, intrinsic viscosities of the parent EPM and some EPM-g-SAN samples as a function of isooctane and MEK contents in solvent mixtures with chlorobenzene.

The continuous line represents the viscometric behaviour of the parent polymer in the two sets of solvent mixtures: the elastomeric chain coil extends on increasing isooctane concentration, thus raising the values of intrinsic viscosity. However the EPM coil decreases its volume up to the separation of EPM elastomer from solvent mixtures containing even low concentrations of MEK. Other curves plotted in *Figure 6* show the viscometric behaviour of two pairs of graft polymers all having a viscometric molecular weight of the elastomeric backbone, $\bar{M}_{v,g}$, of 340 000 but with different SAN/EPM ratios and $[\eta]$ values of the corresponding ungrafted SAN, (*Table 2*). These values have been reported as an indication of the molecular weights of the SAN grafts, e.g. it has been assumed[4-6], that the molecular weight of grafted SAN is equal to that of the ungrafted SAN.

The viscometric behaviour of EPM-g-SAN samples GP 2 and 8 having the lowest SAN/EPM ratio is partially similar to that of the parent polymer.

These samples show a preferential absorption for isooctane and $[\eta]$ increases as the isooctane content of mixtures increases. There is then an inflexion of $[\eta]$ values and finally the precipitation of graft polymers occurs. Isooctane concentrations at which there are $[\eta]$ inflexions

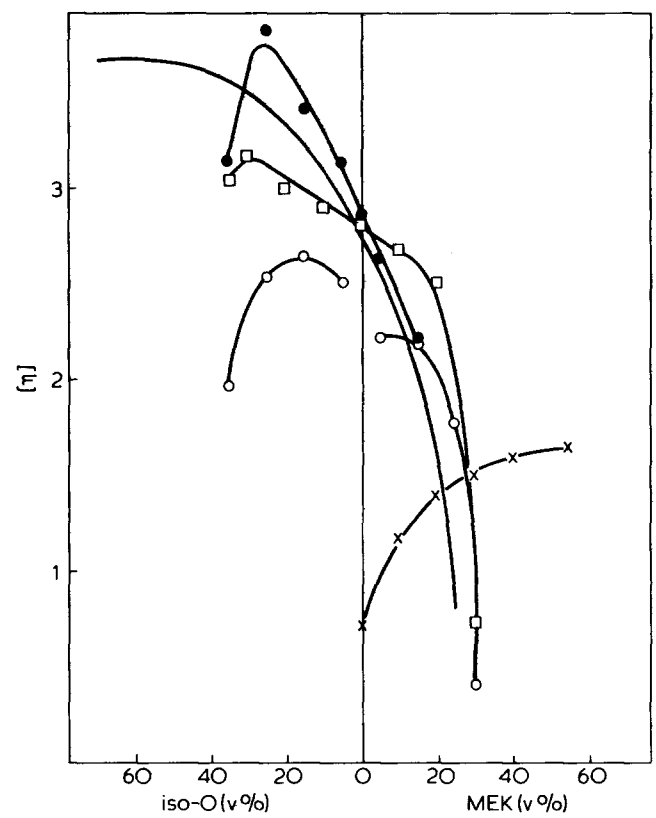

Figure 6 Viscometric behaviour in solvent mixtures with chlorobenzene for two pairs of EPM-g-SAN (●, □ and ○, X) having equal $\bar{M}_{v,g}$, a SAN/EPM of 0.25 and 1 respectively but different SAN branch length. Continuous line represents behaviour of parent polymer (EPM)

Table 2 Molecular data for two pairs of EPM-g-SAN samples having equal $\bar{M}_{v,g}$ and SAN/EPM ratio

Sample	SAN/EPM	$[\eta]^{30°}_{THF}$ of graft polymer	$[\eta]^{30°}_{MEK}$ of ungrafted SAN
GP 2	0.25	3.2	0.4
8	0.27	2.9	0.8
9	1.1	2.5	0.5
5	1.0	1.7	1.5

and graft polymer precipitation are usually dependent on SAN content and molecular weight of the grafted SAN branches.

The addition of MEK to chlorobenzene solutions generally brings about firstly a rapid decrease of graft polymer dimensions followed by precipitation of graft polymer. The effect of length of the SAN branches on viscometric behaviour of EPM-g-SAN is further indicated by the curves plotted in *Figure 6* for the second pair of samples having a larger SAN/EPM ratio and higher molecular weights than the first pair.

The intrinsic viscosities in chlorobenzene/MEK mixtures of the second sample of this pair are higher than those of the first. This result is probably connected with the higher molecular weight of SAN grafted onto the elastomeric chain and preferentially solvated by MEK.

The third sample (GP 9) is insoluble in pure chlorobenzene but becomes slightly soluble with a small amount of either isooctane or methyl ethyl ketone, displaying a behaviour like the previous two samples. The last sample is soluble only in mixtures containing methyl ethyl ketone until a sudden precipitation of the graft elastomer occurs. As a result, the viscometric behaviour of EPM-g-SAN graft polymer in the chosen solvent mixtures is strongly dependent on content and molecular weight of SAN grafted onto EPM backbone.

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