

High Styrene–Rubber Ionomers, an Alternative to Thermoplastic Elastomers

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ABSTRACT: High styrene rubber ionomers were prepared by sulfonating styrene–butadiene rubber of high styrene content (high styrene rubber) in 1,2-dichloroethane using acetyl sulfate reagent, followed by neutralization of the precursor acids using methanolic zinc acetate. The ionomers were characterized using X-ray fluorescence spectroscopy, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), dynamic mechanical analysis (DMA), and also by the evaluation of mechanical properties. The FTIR studies of the ionomer reveal that the sulfonate groups are attached to the benzene ring. The NMR spectra give credence to this observation. Results of DMA show an ionic transition (T_i) in addition to glass–rubber transition (T_g). Incorporation of ionic groups results in improved mechanical properties as well as retention of properties after three cycles of processing. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2294–2300, 2002

Key words: ionomers; glass transition; recycling; mechanical properties

INTRODUCTION

Ionomers are polymers in which ionic domains act as physical crosslinks.^{1,2} Ionomers exhibit attractive physical properties. The properties of ionomers are dependent on the type of polymer backbone, ionic content, type of cation, and the degree of neutralization.^{3,4} The ion containing elastomers based on ethylene propylene diene monomer rubber (EPDM), nitrile–butadiene rubber (NBR), polychloroprene rubber (CR), styrene–butadiene rubber (SBR), and nitrile rubber (NR) have been reported.^{5–9} The introduction of relatively low levels of zinc sulfonate groups into high styrene rubber (HSR) yields ionomers with improved mechanical properties comparable with those of other commercial ionic elastomers, which

could be attributed to the very strong intermolecular association and relatively high stability of metal sulfonate groups.^{10,11} Zinc sulfonated high styrene rubber (ZnS-HSR) has the unique ability to behave as a crosslinked elastomer at ambient temperatures and to undergo melt flow behavior at elevated temperatures as with thermoplastics. It functions as a thermoplastic elastomer and thus could be processed by thermoplastic processing techniques. It has the potential to emerge as an important industrial polymer. The objective of the present work was to synthesize and investigate the properties of ionomers based on high styrene rubber.

EXPERIMENTAL

Materials

Styrene–butadiene rubber of high styrene content (abbreviated as HSR; Powerene-958, bound

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Table I Results of XRF Analysis

Sample	Amount of Sulfur (wt %)	Sulfonate Content (mequiv/100 g polymer)
ZnS-HSR-1	0.339	10.6
ZnS-HSR-2	0.653	20.4
ZnS-HSR-3	1.101	34.4

styrene, 52%) was obtained from Apar Industries (Mumbai, India). 1,2-Dichloroethane (DCE), acetic anhydride, and zinc acetate were obtained from S.D. Fine Chemicals (Mumbai, India). Concentrated sulfuric acid, isopropanol, and methanol were procured from E. Merck (Mumbai, India).

Synthesis of Ionomer

The high styrene rubber (HSR) was dried under vacuum at 50°C for 48 h before use. A 20-g sample of polymer was dissolved in 400 mL of DCE and cooled below 10°C. The sulfonating reagent (acetyl sulfate) was generated in a separate vessel by mixing acetic anhydride and sulfuric acid (98%) in the molar ratio of 1.4 : 1 at 0°C. Subsequently, the reagent (acetyl sulfate) was diluted by DCE. The sulfonating reagent was added slowly, with stirring under nitrogen atmosphere below 10°C. After complete addition, the cooling system was removed and the solution was stirred vigorously for 0.5 h and then the reaction was terminated by adding 20 mL isopropanol. Stirring was continued and a stoichiometric amount of zinc acetate in methanol was added for the neutralization of the polymer sulfonic acid. The product was recovered by steam stripping and was washed several times with deionized water (until reaching neutral pH). The ZnS-HSR was then vacuum dried at 50°C for 48 h. HSR of various concentrations of sulfonic acid contents could be prepared by varying the acetyl sulfate concentrations. This ionic polymer is hereafter represented as xy ZnS-HSR, where xy shows the number of milliequivalents of sulfonic acid/100 g of high styrene rubber.

Sample Preparation

The ionomers were mixed in a Brabender Plasticorder model PL-3S (Brabender, Duisberg, Germany). Mixing was done for 5 min at a rotor speed of 60 rpm, at a temperature of 120°C. Test specimens were prepared by molding in an electrically

heated hydraulic press for 5 min at 150°C under a pressure of 10 MPa.

Characterization Techniques

X-ray Fluorescence Measurements

The sulfur content of the ionomers was estimated as per ASTM D-4294 (1995) using Oxford Lab X-3000 bench-top X-ray fluorescence analyzer supplied by Oxford Instruments (Oxford, UK).

FTIR Analysis

Infrared spectroscopic studies of the compression-molded thin films were taken in a Nicolet Avtar 360 ESP FTIR spectrometer (Nicolet Instruments, Madison, WI), with a resolution of 4 cm^{-1} .

NMR Spectroscopy

NMR spectra of HSR and ZnS-HSR were taken in a Bruker Avance DPX 300 NMR spectrometer (Bruker Instruments, Billerica, MA), operating at a proton resonance frequency of 300 MHz.

Dynamic Mechanical Analysis

The dynamic mechanical analyses of the samples were performed in a dynamic mechanical thermal analyzer (DMTA-MK-II) at a frequency of 10 Hz, and a dynamic strain of 64 μm . The measurements were carried out over a temperature range of -60 to +60°C at a heating rate of 3°C min^{-1} .

Measurement of Mechanical Properties

The stress-strain properties were determined according to ASTM D-412-98a using dumbbell-shape test pieces in an Instron Universal Testing Machine (UTM, model 4206), using a crosshead speed of 500 mm min^{-1} . Tear resistance was determined as per ASTM D-624-98 using unnicked 90°-angle test pieces (die C) at 25°C using a crosshead speed of 500 mm min^{-1} in an Instron UTM, model 4206. A Shore D-type durometer was used to measure the hardness as per ASTM D-2240-97.

Determination of Reprocessability

The reprocessability of the ionomer at level of sulfonation 30 mequiv (100 g polymer) $^{-1}$ was studied by masticating the molded samples in the Brabender Plasticorder for 5 min at a rotor speed of 60 rpm at 120°C. The sample was molded in an electrically heated hydraulic press for 5 min at 150°C, under a pressure of 10 MPa. The process of

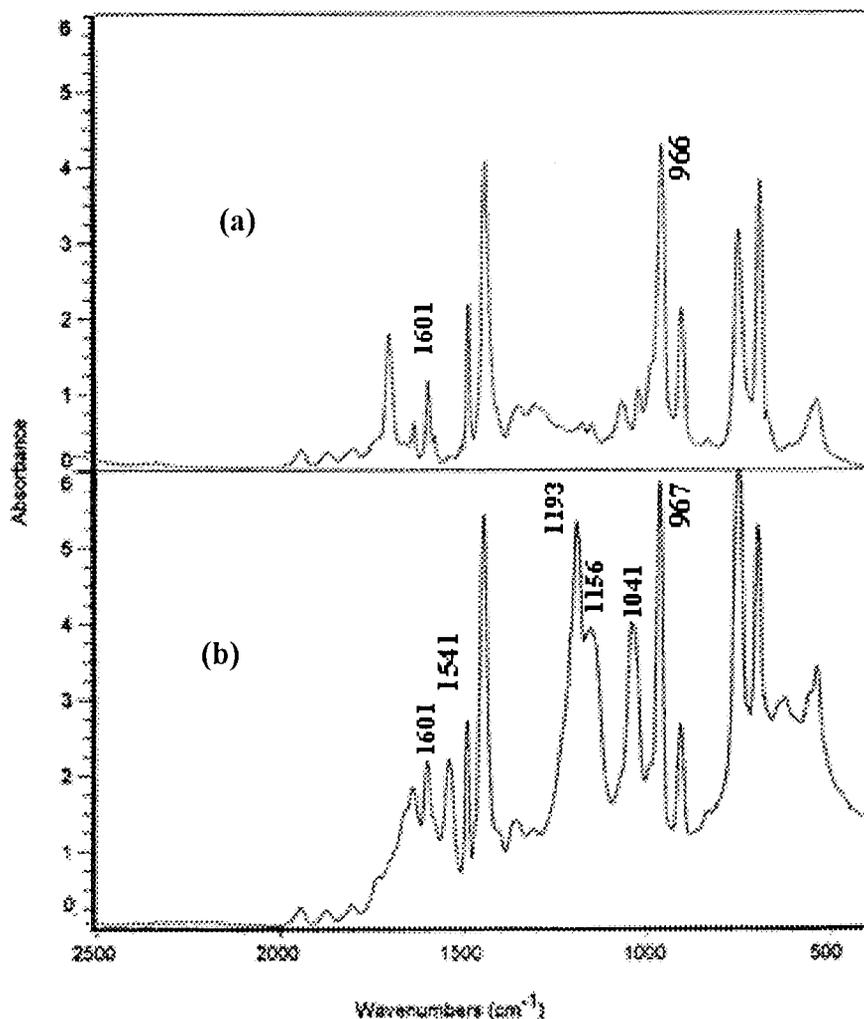


Figure 1 Infrared spectra of (a) high styrene rubber, (b) zinc sulfonated high styrene rubber.

mastication and molding was repeated up to three cycles. The stress-strain properties of the molded specimen after each cycle were determined.

RESULTS AND DISCUSSION

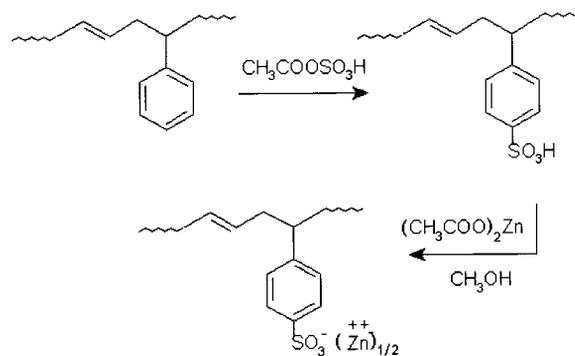
Estimation of Sulfur

The weight percentage of sulfur in the samples and the corresponding level of sulfonation in mequiv $(100 \text{ g polymer})^{-1}$ are shown in Table I. The ionomer samples became harder as the level of sulfonation increased.

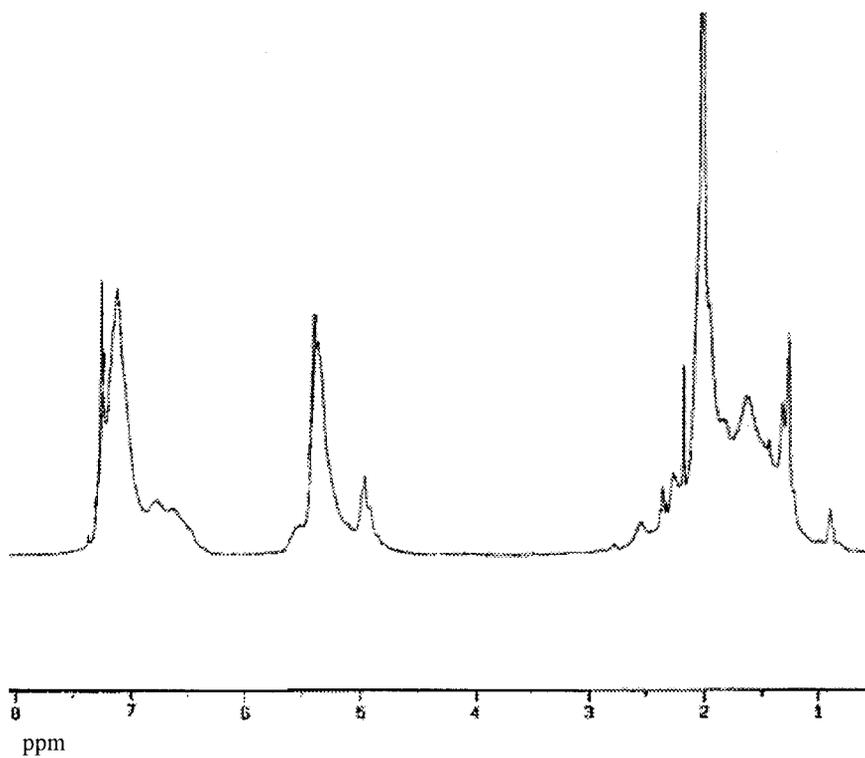
FTIR Characterization

The infrared spectra $(2000\text{--}500 \text{ cm}^{-1})$ of neat HSR and the ionomer prepared from it are shown

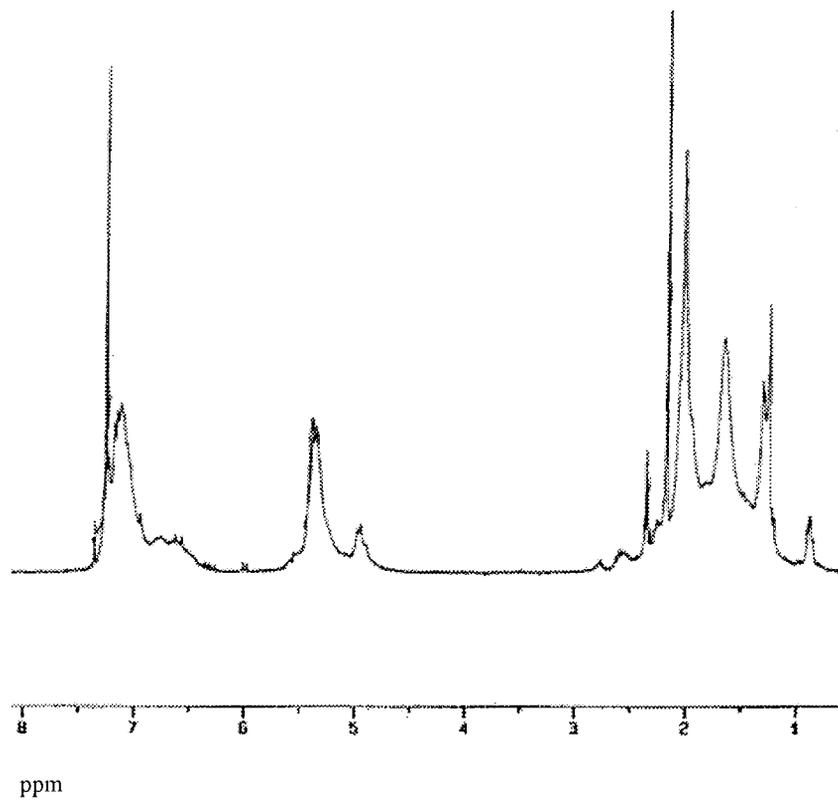
in Figure 1. The spectrum of HSR [Fig. 1(a)] shows a peak at around 1601 cm^{-1} that is characteristic of C=C stretching in the benzene ring.



Scheme 1 Sulfonation reaction on high styrene rubber.



(a)



(b)

Figure 2 NMR spectra of (a) high styrene rubber, (b) zinc sulfonated high styrene rubber.

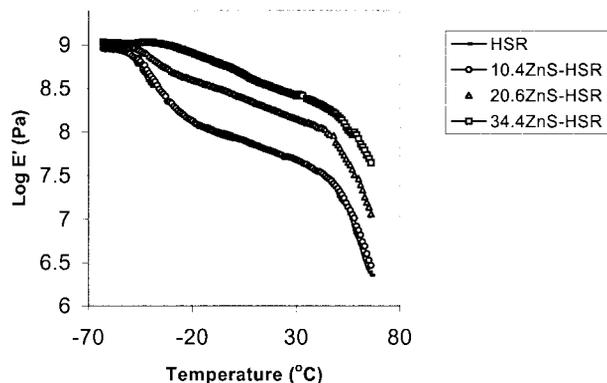


Figure 3 Variation of $\log E'$ versus temperature for the HSR and various ionomers.

The peak at 966 cm^{-1} corresponds to C—H out-of-plane deformation of C=C of butadiene units.¹² Figure 1(b) shows the IR spectrum of the ionomer based on HSR. The peak at 1041 cm^{-1} is assigned to the symmetric stretching vibration of the sulfonate anion attached to a phenyl ring, and the other peaks at 1156 and 1193 cm^{-1} correspond to the asymmetric stretching of the sulfonate groups.^{13,14} The peak at 1541 cm^{-1} represents the disubstituted benzene ring.¹² The peak at 967 cm^{-1} , corresponding to C—H out-of-plane deformation of C=C of butadiene units, is also retained.

There are two kinds of reactive sites in the HSR: (1) the phenyl rings in the styrene units, and (2) the residual C=C in the rubber block. Although olefinic unsaturation is inherently more reactive than the phenyl rings to acetyl sulfate, the larger excess of the phenyl rings (bound styrene is 52%) favors the sulfonation of styrene units.¹³ Infrared spectroscopic analysis confirmed that sulfonation occurred almost exclusively in the styrene units, as proposed in **Scheme 1**.

NMR Spectroscopy

The NMR spectra of the base HSR and ZnS-HSR are represented in Figure 2(a) and 2(b), respectively. In the spectrum of HSR [Fig. 2(a)] the signals corresponding to the aliphatic protons (2 ppm) aromatic protons (7 ppm) are present. In Figure 2(b) (ZnS-HSR), the same signals are retained, although the signals corresponding to the aromatic protons appear shifted. The shifts in the position of benzene protons may be attributed to the sulfonation.^{9,15} The peaks at 7.13 and 7.26 ppm [Fig. 2(a)] in the base material have been shifted to 7.26 and 7.36 ppm [Fig. 2(b)], respectively. This shift in the resonance signals of the phenyl ring confirms that a strong ionic group like $-(\text{SO}_3)_2\text{Zn}$ is attached to the benzene ring.⁹ It can therefore be considered as supplementary evidence for the FTIR spectroscopic observation.⁹

Dynamic Mechanical Analysis

Variation of dynamic mechanical properties with temperature gives information about different transitions in polymers. Figure 3 shows the variation of storage modulus (E') versus temperature for the base materials and their ionomers. Compared with the base polymer the ionomer shows a higher storage modulus resulting from the physical crosslinking arising from ionic aggregates.¹ The values of $\log E'$ at 25°C are given in Table II.

Figure 4 shows the plot of loss tangent ($\tan \delta$) against temperature obtained from the dynamic mechanical analyses of neat HSR and its ionomers. The glass-transition temperature (T_g) occurred around -39°C in the case of HSR. Incorporation of ionic groups causes a shift in the T_g toward the higher side (-37°C). The $\tan \delta_{\max}$ (i.e., $\tan \delta$ value at T_g) was higher for HSR compared to that of its ionomers. The lower value of $\tan \delta_{\max}$ for the ionomers may be attributed to the stiffen-

Table II Results of Dynamic Mechanical Analyses

Sample	T_g^a ($^\circ\text{C}$)	Tan δ at T_g	Transition Due to Ionic Aggregates ^b T_i ($^\circ\text{C}$)	Tan δ at T_i	Log E' at 25°C (Pa)
HSR	-39	0.335	—	—	7.713
10.6ZnS-HSR	-37	0.315	—	—	7.716
20.4ZnS-HSR	-37	0.2050	-4 to +8	0.1486	8.199
34.4ZnS-HSR	-37	0.15	+1 to +30	0.1306	8.461

^a From $(\tan \delta)_{\max}$ in the plot of $\tan \delta$ versus temperature.

^b From $\tan \delta$ versus temperature plot.

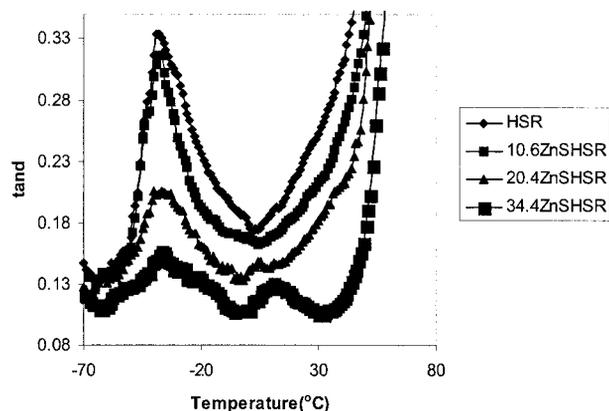


Figure 4 Variation of $\tan \delta$ versus temperature for HSR and various ionomers.

ing imparted by the ionic domains.¹⁶ The $\tan \delta_{\max}$ decreased as the concentration of ionic groups increased. 20.4ZnS-HSR and 34.4ZnS-HSR show additional transitions in the temperature range of -4 to $+8^\circ\text{C}$ and $+1$ to $+30^\circ\text{C}$, respectively, which are ascribed to the presence of a second phase arising out of the immobile segments or restricted mobility region adjacent to the ionic domains (T_i).¹⁷ Transition attributed to ionic aggregates has been found to occur in the case of rubbery ionomers.^{2,16,18} In the case of HSR, and 10.6ZnS-HSR, as expected, the broad transition attributed to ionic aggregates has not been observed. The absence of clear ionic transition in the case of 10.6ZnS-HSR may be the result of the low ion content.^{3,4} In the region of low ion concentration the ions are assumed to exist in the form of multiplets.¹⁹ Given that the ionomers are not chemically crosslinked, they became soft at elevated temperature.¹⁰ The results of dynamic mechanical analysis are summarized in Table II.

Mechanical Properties

The mechanical properties of neat HSR and its ionomers are summarized in Table III. Incorpora-

tion of ionic groups caused a gradual increase in modulus and tensile strength and a decrease in elongation at break. This is because of the fact that ionic groups phase separate into spherical ion-rich domains, acting as physical crosslinks.²⁰ The tear strength of elastomers is a measure of crack propagation. It is known that tear strength is enhanced by factors that tend to dissipate energy.²¹ ZnS-HSR shows higher tear strength than that of the base HSR. Tear strength values of ionomers increase with incorporation of ionic groups. The ionic groups of ZnS-HSR may be acting as tear deviators. Incorporation of ionic groups increased the hardness of ZnS-SBR. Hardness is a measure of the modulus of elasticity at low strain.²² As expected, hardness and abrasion resistance increased as the ionic content increased. Enhancement in mechanical properties is thought to arise from the presence of a small, coherent second phase that behaves like ultrafine particles of reinforcing filler in addition to acting as multifunctional crosslinks.^{23,24}

Reprocessability

Results of reprocessability studies are shown in Figure 5. It was observed that the stress-strain properties of the 34.4ZnHSR samples remained almost constant, even after three cycles of processing. This shows that 34.4ZnS-HSR behaves as a thermoplastic elastomer and could be processed by mechanical recycling without deterioration in physical properties.

CONCLUSIONS

High styrene rubber ionomers of various ionic concentrations could be synthesized. X-ray fluorescence spectroscopy studies could be used to estimate the sulfur content of the ionomer samples. FTIR and NMR spectra provide evidence of

Table III Mechanical Properties at 25°C

Property	Sample			
	HSR	10.6ZnS-HSR	20.4ZnS-HSR	34.4ZnS-HSR
Tensile strength (MPa)	2.62	3.85	8.54	16.81
Modulus at 50% elongation (MPa)	2.43	3.36	8.18	14.98
Elongation at break (%)	131.70	103.75	90.34	78.78
Tear strength (N/mm)	15.48	22.49	57	106
Hardness (Shore D)	15	20	35	45

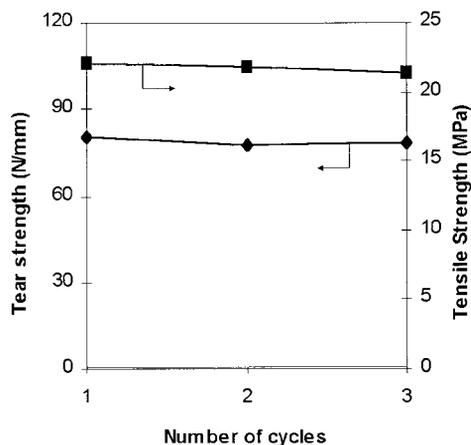


Figure 5 Variation of stress–strain properties of 34.4ZnS-HSR at different cycles of processing.

sulfonation at the styrene units. Results of dynamic mechanical analysis show the occurrence of an ionic transition in 20.4ZnS-HSR and 34.4ZnS-HSR, in addition to the glass–rubber transition of the base polymer. Ionomers show improved mechanical properties compared to those of the base polymer. The thermoplastic elastomeric nature of the chemically modified sample is evident from the retention of stress–strain properties after repeated mechanical recycling.

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