Polymerization of Vinyl Chloride in Presence of Substituted Olefins: Effects on Molecular Weight and Melt Rheology

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Synopsis

Vinyl chloride (VCM) was polymerized by free-radical suspension procedures in presence of methyl-substituted olefins such as propylene, isobutylene, *cis*-2-butene, trimethylethylene, and tetramethylethylene. Dilute solution viscosities of polymer formed in the presence of these olefins were measured and compared to that of trichloroethylene, a chlorinated chain-transfer agent. A pseudo-chain-transfer coefficient for these olefins was calculated based on solution viscosity determinations and found to be exponentially proportional to the number of allylic hydrogens. The effects on melt flow of the olefin distribution in the polymer chain were examined. Olefins at the ends of polymer chains were found to have no effect on melt rheology, whereas those in internal portions of chains were found to significantly increase melt flow.

INTRODUCTION

Chain transfer as a mode of reducing polymer chain length in a radical polymerization was first suggested by Flory.[1] Subsequent studies by Mayo[2] quantitatively defined the effects of various parameters on kinetic chain length of polymers. Graphical interpretations of data by Palit et al.,[3] Allen et al.,[4] and Baysal et al.[5] have been used to determine the effects of chain transfer to monomer and initiator and the effect of polymerization rate. For precision these chain-transfer coefficients (CTCs) were calculated in polymerization systems where the conversion was maintained at less than 10%.

Polymerization of vinyl chloride has been examined by various groups.[6,7] Effects of temperature and initiator level on molecular weight of PVC were determined. Recent work by Cottman[8] demonstrated that the molecular weight of PVC changed as a function of conversion. Hamielec[9] had gathered experimental evidence indicating that the level of initiator had little effect on the molecular weight of PVC. Ravey[10] has indicated that there was a relationship between the temperature of polymerization (T_p) and dilute solution viscosity when studied at high conversion (50–80%), but never considered the effects of initiator level. In addition, studies of the copolymerization of VCM with other monomers indicate that both composition and molecular weight change as a function of conversion,[11,12] except in very special cases such as comonomer azeotropes[13] or charge-transfer systems.[14]

Commercial grades of suspension PVC are usually polymerized to conversion levels of 70–90%. In our study of polymerization of VCM in the presence of olefins, we were not able to measure a true CTC, since the composition of the monomer mixture and rate of polymerization were changing over the range of polymerization examined.[12] A pseudo-chain-transfer coefficient was calculated

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for these substituted olefins using a modified procedure described by Mayo.[2] The pseudo-chain-transfer coefficient is taken as the slope of the line plotting reciprocal of inherent viscosity $(IV)^{-1}$ in g/dl vs chain-transfer-agent concentration (c_T) in moles/100 moles VCM:

$$\Delta(IV)^{-1}/\Delta C_T$$

An alternative approach in examining the chain transfer of PVC is to plot $(\overline{M}^{-1}$ vs initiator concentration. This is demonstrated in Fig. 2. The extrapolation to zero initiator concentration is the reciprocal of chain transfer to monomer $(C_M)^{-1}$. This is the highest absolute molecular weight obtainable at a given polymerization temperature. This value for PVC at 65°C was found to be $\overline{M}_n = 26{,}700$. This is consistent with the results reported by Abdel-Alim and Hamielec.[9]

Molecular weight distribution for the homopolymers detailed In Table II were examined using the gel-permeation chromatography procedure described by Chan.[21] Lack of any significant skewing in M_w/M_n ratio as the initiator level was increased indicated no unusual chain branching[22] or broadening of the molecular weight distribution. PVC resin has been shown to exhibit a high degree of order in the melt state.[15] This results in difficulties in melt processing PVC. Several approaches have been used to circumvent this problem: use of compounding additive[16] and by modification of the PVC polymer either by changes in molecular weight[17] or by copolymerization.[18]

Heiberger et al.[19] have examined the processability of PVC and found that the introduction of propylene into the polymer chain significantly improved the melt processability of the PVC resin. They concluded that the $-CH_3$ group is isosteric to $-Cl$ from VCM and occupies the same volume in the PVC chain, but does not include the same polar interaction as the $-Cl$ group.[20]

The purpose of this paper is to study changes in molecular weight and in melt rheology of PVC when polymerized under conditions where there are pendant methyl groups along the backbone of the chain and/or when methyl groups are localized at the ends of the chain.

EXPERIMENTAL

Raw Materials. The following materials were used:

Water. Tap water was passed through deionization column and then double distilled under a nitrogen purge.

Suspension agent. Hydroxypropylmethyl cellulose (Methocel K-35) from Dow Chemical was used as received.

Initiator. Lupersol-11 (75% active *t*-butyl perpivalate) supplied by Lucidol was used as received.

Monomer. CP-grade vinyl chloride obtained from Air Products Specialty Gas was used as received.

Comonomer/chain-transfer agents (CTAs). The type of material and its characteristics are noted in Table I. All materials were used as received from the supplier.

Polymerization procedures. We made use of the following procedures:

Reactor. Chemco MDX-GJ, 1.5 l., manufactured by Chemical Equipment Corp. of Tulsa, Oklahoma, temperature control to ±0.5°C.

TABLE I

Properties of Substituted Olefins/TCE

Name	M_w	bp/fp, °C	Density, g/ml	Source	Purity, %
Propylene	42.10	−47/−185	0.519	Air Products	CP grade (99)
Isobutylene	56.12	−7/−140	0.594	Air Products	CP grade (99)
Cis-2-Butene	56.12	+4/−139	0.621	Air Products	CP grade (99)
Trimethylethylene	70.14	+38/−133	0.689	Aldrich	99+
Tetramethylethylene	84.16	+73/−74	0.708	Aldrich	99+ (gold label)
Trichloroethylene	131.40	87/−73	1.4642	Aldrich	98

TABLE II

Effects of Variable Initiator Level on Properties of PVC Resin

Run No.	g/HG[a]	M/HM[b]	IV unit, dl/g	$(IV)^{-1}$	Yield, %	M_w	M_n	$M_n^{-1} \times 10^{+5}$	M_w/M_n	MF, g/10 sec
1	0.053	1.91×10^{-2}	0.770	1.299	84.3	55,250	26,300	3.802	2.10	—
2	0.106	3.81×10^{-2}	0.764	1.309	87	54,450	25,900	3.861	2.10	—
3	0.2125	7.62×10^{-2}	0.726	1.374	87	50,950	24,650	4.057	2.06	—
4	0.425	15.2×10^{-2}	0.689	1.451	86.2	49,250	23,900	4.184	2.01	0.95

[a] g/100 g VCM.

[b] moles/100 moles VCM.

TABLE III

Polymerization at Constant Initiator Level

	Chain Transfer Agent								Gel-Permeation Chromatography		
Run no.	Type	Level, phm	M/HM[a]	IV unit, dl/g	$(IV)^{-1}$	MF, g/10 sec	Cycle time, hrs	Yield, %	M_w	M_n	M_w/M_n
5	TCE	0.488	0.232	0.687	1.456	0.9	1.50	83			
6		0.976	0.464	0.633	1.580	4.0	1.75	82			
7		1.464	0.696	0.597	1.675	7.1	1.75	83			
8	Tri	0.552	0.492	0.626	1.597	4	3.85	75			
9		1.103	0.983	0.531	1.883	26.0	6.25	75			
10	Tetra	0.117	0.87	0.694	1.441	0.8	3.5	73			
11		0.234	0.173	0.651	1.536	1.7	4.75	70			
12		0.351	0.261	0.629	1.590	3.8	5.25	69			
13	C-2B	1.1	1.225	0.615	1.626	4.0	3.5	75			
14		2.0	2.227	0.542	1.845	25.2	5.25	75	27,800	13,400	2.08
15		2.87	3.190	0.494	2.024	50.0	6.75	74			
16	P	1.07	1.584	0.687	1.456	2.1	1.5	79			
17		2.0	2.971	0.669	1.495	3.7	2.25	77			
18		4.03	5.991	0.589	1.698	22.0	3.75	83			
19	iB	1.33	1.48	0.586	1.698	13.8	2.25	79	36,100	17,500	2.06
20		2.07	2.31	0.527	1.898	56	3.0	77	31,800	15,300	2.07
21		2.93	3.26	0.498	2.008	154	3.25	79	24,900	12,200	2.05
22		3.90	4.34	0.438	2.283	270	4.00	83			

Recipe: H_2O = 600 g, VCM 300 g, K-35 0.24 g, 1.01 ml (7.62×10^{-2} moles/100 moles). Abbreviations: TCE = trichloroethylene, Tri = trimethylethylene, Tetra = tetramethylethylene, C-2B = *cis*-2-butene, P = propylene, and iB = isobutylene.

[a] moles/100 moles VCM.

Recipe:

1.	Water	600 g
2.	Methocel K-35	0.24 g
3.	*t*-butyl perpivalate (Lupersol-11)	see Tables II and III
4.	Substituted olefin or trichloroethylene	see Table III
5.	Vinyl chloride	300 g

Charge procedure. Components 1 and 2 were added to the reactor under a nitrogen purge and stirred until dissolved. Components 3–5 were then added rapidly. Reactor contents were quickly heated to 65°C. Polymerizations were carried to the conversion indicated in Tables II and III. At the end of the polymerization, the reactor contents were quickly cooled to ambient, vented to atmospheric pressure, filtered, and dried.

TABLE IV

Psuedo-Chain-Transfer Coefficients for Olefins and TCE[a]

Cis-2-Butene	0.210
Trimethylethylene	0.550
Tetramethylethylene	0.910
Propylene	0.0540
Isobutylene	0.214
Trichloroethylene	0.453

[a] Molar chain-transfer coefficient based on data at fixed initiator level; units: $\Delta(\mathrm{IV})^{-1}$(moles CTA/100 moles VCM).

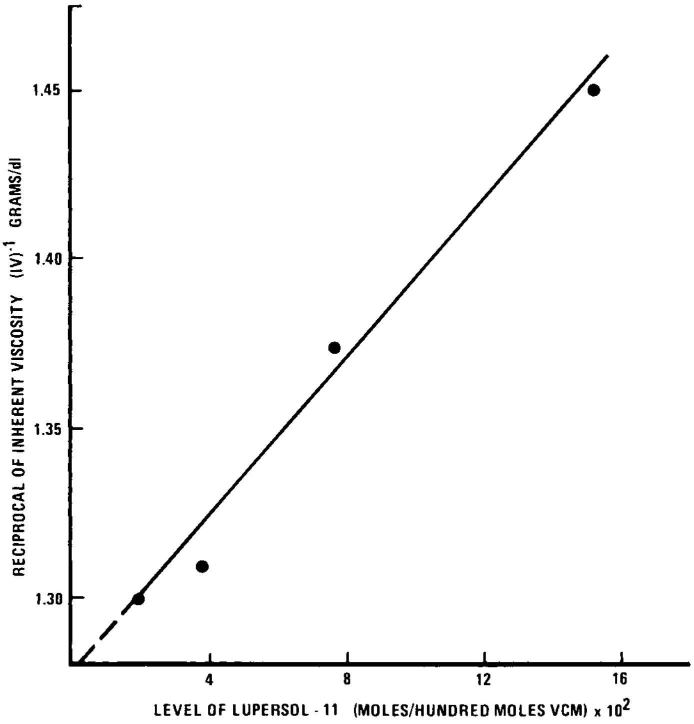

Fig. 1. IV^{-1} of PVC resin as a function of the initiator level (Lupersol-11).

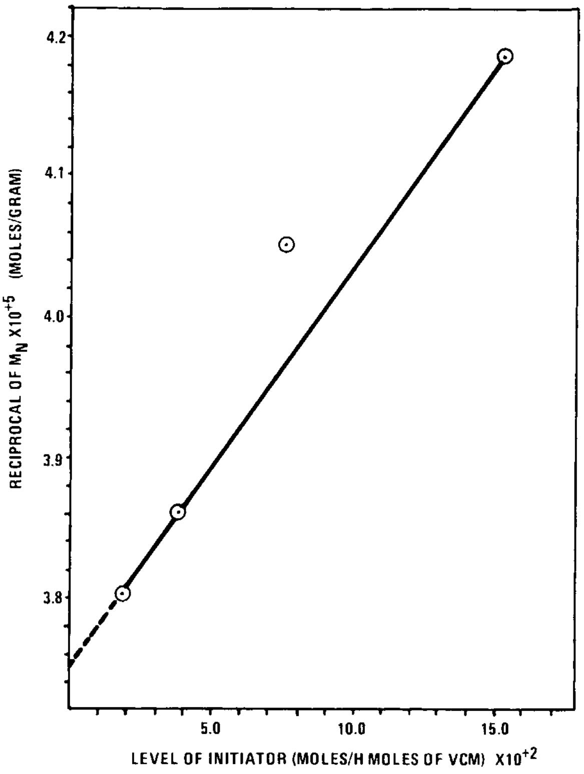

Fig. 2. Reciprocal number-average molecular weight $(\overline{M}_n)^{-1}$ as a function of the initiator level (Lupersol-11).

Test procedures. Inherent viscosity (IV), ASTM Method D-1243-60A, melt flow (MF) ASTM Method D-1238-57-T Condition F. Molecular weight distribution was determined by gel-permeation chromatography.[21]

Discussion

Effect of Initiator Level on Inherent Viscosity of PVC

We have noted that the type and concentration of initiator will have an effect on the molecular weight M_w of a PVC resin; decreasing the M_w as the concentration of initiator is increased. This effect of initiator concentration may be due to two separate factors: chain transfer to the initiator[4] or changes in the rate of polymerization (R_p).[5] A plot of reciprocal of number-average molecular weight $(\overline{M}_n)^{-1}$ as a function of R_p would indicate, if the data fell on a straight line, that chain transfer to initiator was minimal. No attempt was made to determine R_p during the initial 0–5% conversion nor to separate any samples at low conversion for study of M_w as a function of conversion.

A series of PVC homopolymer resins, detailed in Table II, were prepared to determine the magnitude of these two effects—chain transfer to initiator and R_p—in combined form. All polymerizations were carried to 85–87% conversion. A plot of $(\mathrm{IV})^{-1}$ vs the level of initiator indicated (Fig. 1) that level of initiator had a large effect on the inherent viscosity of the PVC.

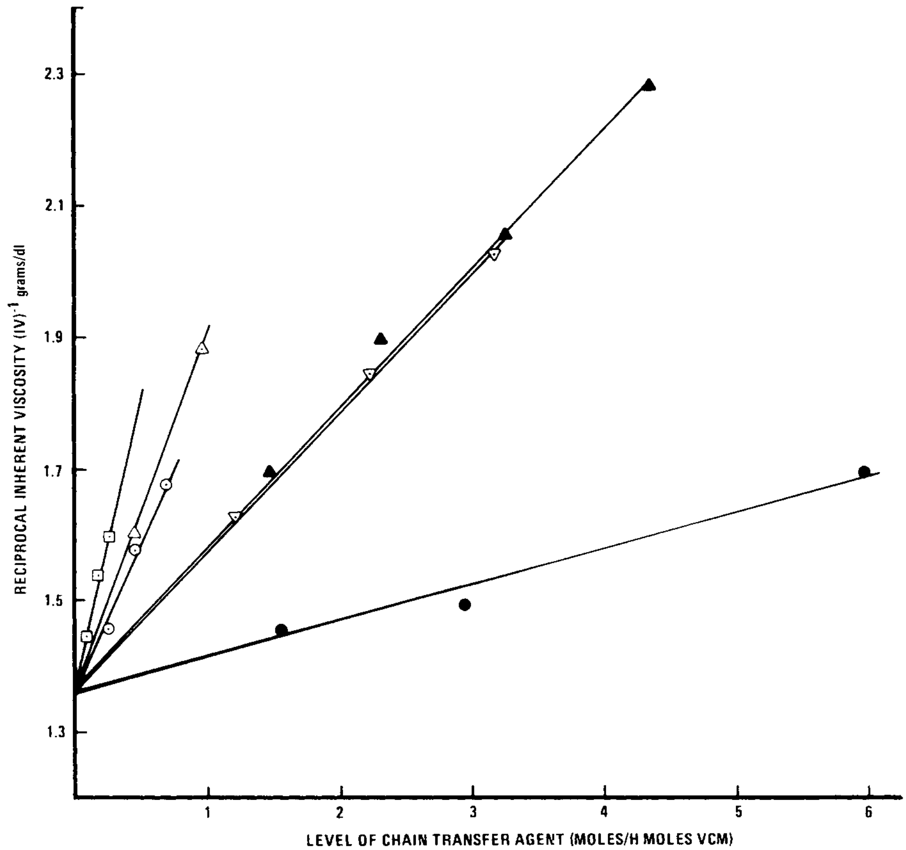

Fig. 3. IV^{-1} of PVC resin as a function of the CTA level: ▲, *cis*-2-butene; △, trimethylethylene; ▽, isobutylene; ● propylene; ○, trichloroethylene; and □, tetramethylethylene.

Effects of Olefins on Inherent Viscosity of PVC

Polymerization of VCM has been studied in the presence of different olefins, e.g., propylene[12,19,20] and isobutylene.[23] Overall reduction in inherent viscosity of PVC polymerized in the presence of these olefins is due to chain transfer of allylic hydrogens on methyl groups.[24]

A series of polymerizations of vinyl chloride were run under conditions described in Table III to determine the influence of olefin concentration on solution viscosity of resins. Polymerizations were all run at a fixed level of *t*-butyl perpivalate; 1 ml/300 g VCM; 7.62×10^{-2} moles/100 moles VCM.

Reciprocal viscosity, (IV),$^{-1}$ is plotted against molar concentration of olefin in Fig. 3. The zero intercept in this figure is based on the homopolymer run at 7.62×10^{-2} moles initiator/100 moles VCM (Run 3). The slopes of these lines relating (IV)$^{-1}$ to the concentration of the CTA are shown in Fig. 4 and are summarized in Table IV.

There is an exponential relationship between the number of allylic hydrogens available in the olefin and the pseudo-chain-transfer coefficient for the olefins. An interesting point is that isobutylene and *cis*-2-butene have the same calculated value for pseudo-chain-transfer coefficient, e.g., 0.210 and 0.214. This would imply that the chain-transfer activity for the two compounds, *cis*-2-butene and isobutylene, are equal. There appears to be little likelihood of a chain-

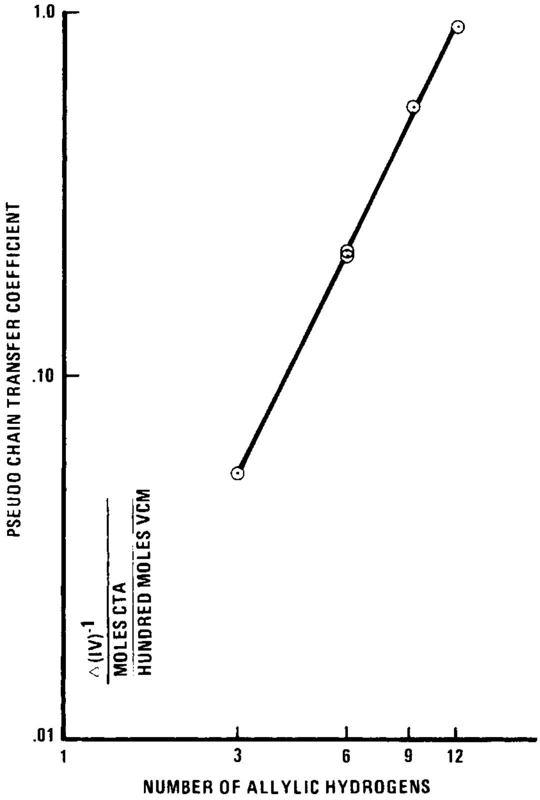

Fig. 4. Pseudo-chain-transfer coefficient for substituted olefins as a function of the number of allylic hydrogens.

transfer reaction to allylic hydrogens once incorporated into a PVC chain, since the molecular weight distributions as determined by gel-permeation chromatography are normal: 2.05–2.10.

Trichloroethylene was used as a comparative standard. Our data show that the transfer coefficient for this chlorinated olefin is very similar to that of trimethyl ethylene.

Effects of Olefins on the MF of PVC

Copolymerization of PVC with olefins such as propylene[25] and isobutylene[23] have been previously examined. The reactivity ratio of substituted olefins with VCM have been studied by nmr techniques.[26] In that study it was found that hindered α-olefin, such as trimethylethylene, did not polymerize into a growing PVC chain. The MF and IV of PVC polymerized in the presence of propylene have been shown to vary with conversion.[12] To minimize the effects of different conversions, we have carried the polymerization to high conversion. These data are summarized in Table III.

The logarithmic MF of these resins is graphically represented as a function of IV in Fig. 5. In this figure we have three distinct sets of linear relationships:

1. PVC resin prepared in presence of "nonpolymerizing" olefins or TCE. These PVC resins were prepared in the presence of *cis*-2-butene, -trimethylethylene, tetramethylethylene, and trichloroethylene.

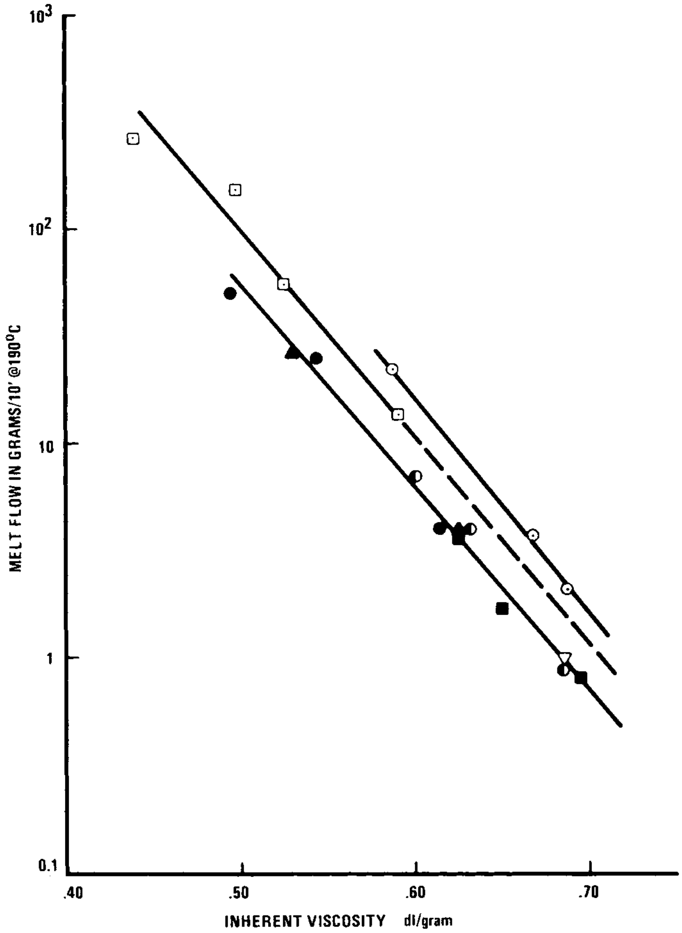

Fig. 5. MF as a function of IV for PVC resin prepared in the presence of CTAs: ○, propylene; □, isobutylene; ●, cis-2-butene; ■, trimethylethylene; ■, tetramethylethylene; ◐, trichloroethylene; ▽, homopolymer.

2. PVC resin prepared in presence of "polymerizing" olefins. PVC resins prepared in presence of isobutylene and propylene form two distinctly different MF/IV relationships when compared to the nonpolymerizing olefins. These olefins do copolymerize into the PVC chain as well as chain transfer to reduce the molecular weight of growing PVC chain. The enhanced MF of PVC prepared in the presence of these polymerizing substituted olefins is due to a disruption of the ordered melt state[15] in PVC by the presence of methyl groups throughout the polymer chain. The advantage of propylene as a MF modifier when compared to isobutylene is due to the fact that in isobutylene all methyl groups are not randomly distributed, rather, half are in a vicinal distribution.

CONCLUSIONS

1. The IV of PVC resin can be reduced by polymerizing VCM in the presence of olefins with allylic hydrogens.
2. The reduction in IV at high conversion can be related to the number of allylic hydrogens in the olefin, and a pseudo-chain-transfer coefficient can be calculated for these olefins.

3. The MF of PVC prepared in the presence of these olefins is affected by the distribution of the olefin in the PVC chain. The olefins attached at the ends of the PVC chain have no effect on increasing MF properties.

a. Olefins incorporated within the chain increase MF by disrupting the melt order of the PVC chains.

b. Because of its more random separation of methyl groups propylene is a better agent for increasing MF than isobutylene when compared at equal molecular weight (IV).

4. The initiator concentration has a marked effect on the IV of PVC.

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