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New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers)

22. Synthesis and Characterization of Linear and Three-Arm Star Block Copolymers of Isobutylene and N-Acetylethyleneimine

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SUMMARY

Linear and three-arm star tosyl-telechelic polyisobutylenes (i.e., PIB's carrying two and three p-toluene-sulfonic acid ester end groups, respectively) have been synthesized and characterized by a variety of techniques. Subsequently these prepolymers were used as macroinitiators for the ring opening polymerization of 2-methyl-2-oxazoline leading to linear poly(N-acetylethyleneimine-b-isobutylene-b-N-acetylethyleneimine) and three-arm star poly(N-acetylethyleneimine-b-isobutylene). High yields (78-98%) and blocking efficiencies (70-80%) have been obtained. The absence of free polyisobutylene in the product indicates highly efficient initiation of 2-methyl-2-oxazoline polymerization by the tosyl-telechelic polyisobutylene. The less than 100% blocking efficiencies are probably due to chain transfer to 2-methyl-2-oxazoline. Hydrolysis of these block copolymers yielded poly(ethyleneimine-b-isobutylenes).

INTRODUCTION

Previous papers from this laboratory concerned the synthesis of linear telechelic (α,ω-difunctional) polyisobutylenes carrying exactly two terminal tertiary chlorines (KENNEDY and SMITH, 1980), isopropenyl groups (KENNEDY et al., 1979) or primary alcohols (IVAN et al., 1980). Recently three-arm star telechelic polyisobutylenes having three functional groups at the chain ends have been obtained (KENNEDY et al., 1981). These linear and three-arm star telechelic polyisobutylenes are valuable intermediates for further modifications and derivatizations.

In the course of our fundamental investigations on sequential copolymers it appeared of interest to prepare linear and star-block copolymers comprising water insoluble, e.g., polyisobutylene, and water soluble sequences, e.g., poly(N-acetylethyleneimine) and/or polyethyleneimine. We proposed to reach this objective by synthesizing block copolymers of 2-oxazoline (or its derivatives) and polyisobutylene; the subsequent hydrolysis of the polyoxazoline sequence to polyethyleneimine sequence also promised to be of interest. The N-acetylethyleneimine/isobutylene block copolymer was thought to be obtainable by initiating the polymerization of 2-methyl-2-oxazoline (2-Me-2-Ox) with suitably modified (for example, tosyl) telechelic polyisobutylenes. The initiation of 2-oxazoline polymerization by macromolecules carrying pendant p-toluene sulfonic acid esters (SAEGUSA and IKEDA, 1979; PERCEC, 1981; SIMIONESCU et al., 1982) or haloalkyl groups (SAEGUSA et al., 1978; SEUNG and YOUNG, 1979, 1980; MORISHIMA et al., 1981) has been described

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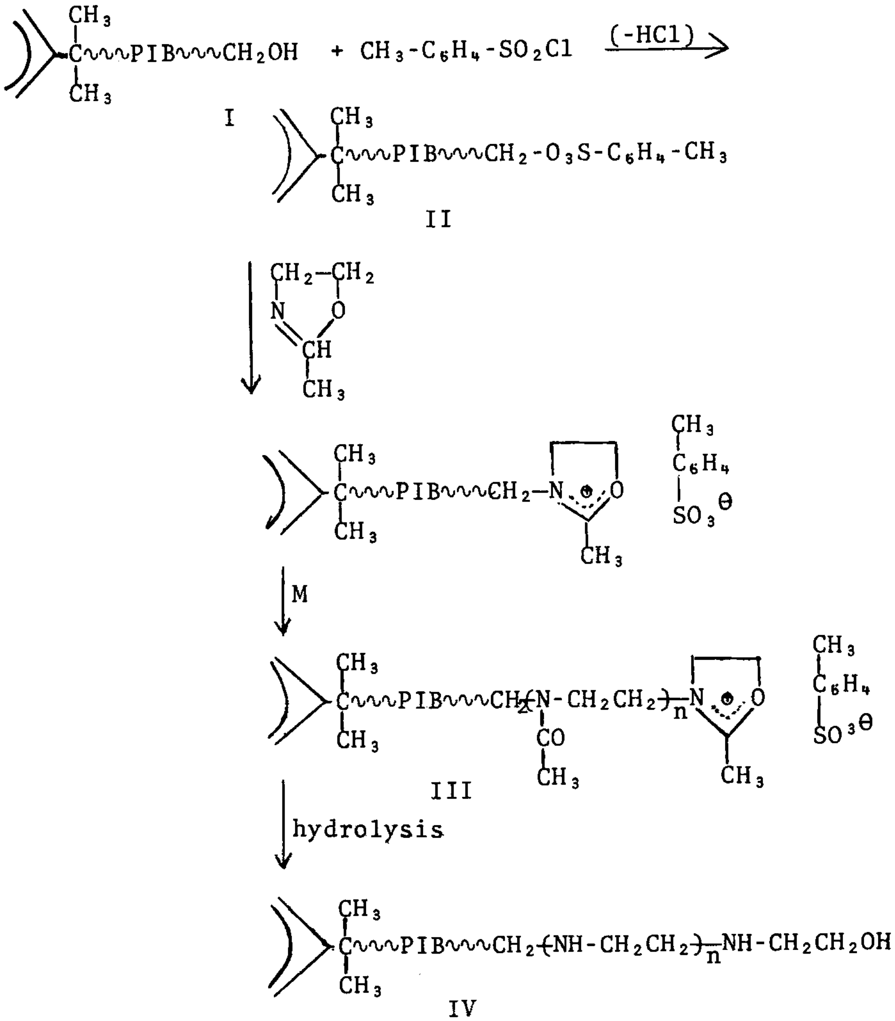
This paper concerns the synthesis of linear and three-arm star tosyl-telechelic PIB's, their use to initiate the cationic ring opening polymerization of 2-Me-2-Oxz to produce amphiphylic N-acetylethyleneimine/isobutylene block copolymers, and their hydrolysis to yield ethyleneimine/isobutylene block copolymers. Scheme 1 helps visualize the conversions explored.

Scheme 1: Synthesis of N-Acetylethyleneimine/Polyisobutylene and Ethyleneimine/Polyisobutylene Block Copolymers



The symbol $\rangle\rangle$-$C(CH_3)_2$ - indicates two or three branches emanating from a central inifer residue, i.e., a 1,4 or 1,3,5 substituted phenyl ring.

EXPERIMENTAL

A. Materials. 2-Me-2-Oxz (Aldrich) was dried over molecular sieves (4 Å) and distilled under reduced pressure before use.

N,N-dimethylformamide (Aldrich, spectrophotometric grade) was dried over molecular sieves (4 Å)and distilled under dry nitrogen. Toluene (Aldrich) was refluxed several days over sodium and distilled under nitrogen. Methylene chloride was distilled over CaH_2 under nitrogen. Triethylamine (Eastman) and pyridine (Aldrich) were dried over KOH.p-Toluenesulphonylchloride (Eastman) and 4-N,N-dimethylaminopyridine (Aldrich) were used as received. Two samples of α,ω-di(hydroxy)polyisobutylene (KENNEDY, 1980, 1979; IVAN et al., 1980) and a three-arm star telechelic polyisobutylene carrying primary alcohol end groups (KENNEDY et al., 1981) were synthesized. Characterization data of the starting materials are shown in Table 1.

Table 1

Characterization of Starting Telechelic Prepolymers

	PIB-Alcohol	PIB-Tosylate	$\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{F}_n$	$\bar{F}_n$
1	linear PIB-diol		3,200		1.7		2.0	
1a		linear PIB-tosylate		3,400		1.6		2.0
2	linear PIB-diol		4,780		1.72		2.0	
2a		linear PIB-tosylate		6,100		1.4		2.0
3	three-arm star PIB-triol		16,500		1.8		3.0	
3a		three-arm PIB tosylate		17,000		1.6		3.0

B. Techniques. ^{1}H-NMR analysis was carried out by using a Varian T-60 NMR spectrometer at room temperature, CCl_4 or $CDCl_3$ solutions and TMS as internal standard. A Perkin-Elmer 521 infrared spectrophotometer was used to record IR spectra of polymer films on KBr pellets. Molecular weights were determined by GPC using a Waters Associated 6000 A (high pressure) pump, UV and RI detectors and micro Styragel columns of 10^6, 10^5, 10^4, 10^3, 500 Å, and a calibration plot constructed with polyisobutylene standards. Glass transition temperatures Tg were determined by a duPont Thermal Analyzer 990 on 15-20 mg samples at a 10°C/min heating rate. Transmission electron micrographs of these films casted from $CHCl_3$ solution were obtained on a JEOL-Model 120 instrument.

C. Synthesis of Linear and Three-Arm Star Tosyl-Telechelic PIB's. A representative tosylation was carried out as follows: A solution of tosyl chloride (1.0 g, 5.24 mmole) in 10 ml CH_2Cl_2 was added dropwise to a stirred mixture of linear telechelic (I) (4.2 g, 1.31 mmole, $\bar{M}_n$= 3,200, $\bar{M}_w/\bar{M}_n$= 1.7, 2.62 mmole-OH), 4-N,N-dimethylaminopyridine (0.64 g, 5.24 mmole), triethylamine (5 ml, excess) and CH_2Cl_2 (15 ml). The mixture was stirred at 20°C for 10 hours, after which the solution was washed sequentially with water, 10% HCl, water, aqueous $NaHCO_3$,water. Then the solution was dissolved in hexanes and reprecipitated three times from hexanes solution into acetone. After each precipitation the polymer functionality was checked by ^{1}H-NMR. After the second precipitation, the polymer functionality remained constant. The final purification was done by washing the hexanes solution of the polymer several times with water (to remove acetone), drying over anhydrous $MgSO_4$ and molecular sieves (4 Å). Finally the solvent was evaporated and the polymer was dried in vacuum at room temperature for two days, $\bar{M}_n$ = 3,400, $\bar{M}_w/\bar{M}_n$ = 1.6, $\bar{F}_n$ = 2.0 by ^{1}H-NMR.

D. Preparation of N-Acetylethyleneimine/Isobutylene Block Copolymers. Mixtures of 2-Me-2-Oxz, tosylate-telechelic polyisobutylene, DMF and toluene were subjected to few freeze-thaw cycles in an ampoule under vacuum. After 16-50 hrs. of polymerization in sealed ampoules at 100-120°C (see Table 2) charges were then cooled and the presence of unreacted 2-Me-2-Oxz was determined by ^{1}H-NMR spectroscopy. Polymerizations were terminated by the addition of a few drops of methanol and the volatile components were evaporated. The composition of the crude product was determined by ^{1}H-NMR.

Table 2

Synthesis of N-Acetylethyleneimine/Isobutylene Block Copolymers [Solvent System: Toluene/DMF=4/1(v/v; solvent/sum of 2-methyl-2-oxazoline plus tosyl-telechelic polyisobutylene = 3/1 (v/w)]

Expt.	PIB-Ts mmole	$\bar{F}_n$	2-Me-2-Oxz mmole	Temp. °C	Time hrs.	Conv. of 2-Me-Oxz	$\overline{DP}_n$ of 2-Me-2-Oxz Block	$\overline{DP}_n$ of $\bar{M}_n$ of PIB Tosylate	$B_{eff.}$ %
1	0.2	2.0	54.2	120	50	98*	97	61	70
2	0.11	2.0	29.3	100	16	78.4	77	109	79.5
3	0.027	3.0	15.0	120	20	83.0	112	101	98.0

*Calculated from overall composition data

Then the polymer was dissolved in chloroform, precipitated into diethyl ether, filtered, dried and the yield was determined gravimetrically. The composition of the precipitated product (by ^{1}H-NMR) did not change. Evaporation of the ethyl ether/chloroform mother-liquor did not produce additional polymeric material.

E. Preparation of Ethyleneimine/Isobutylene Block Copolymers (IV in Scheme 1) by Alkaline Hydrolysis of III.
Poly(N-acetylethyleneimine-b-isobutylene-b-N-acetylethyleneimine)was heated with an aqueous NaOH solution (2.5 molar excess relative to the N-acetylethyleneimine concentration in the block copolymer) at 100°C for 40 hours. After cooling poly(ethyleneimine-b-isobutylene-b-ethyleneimine) was obtained as white precipitate. It was filtered, washed with water till neutral and dried under vacuum at 50°C.

RESULTS AND DISCUSSION

As outlined in Scheme 1 the first phase of this research concerned the synthesis of N-acetylethyleneimine/isobutylene block copolymers by initiating the polymerization of 2-Me-2-Oxz with tosyl-telechelic PIB macroinitiators. Subsequent deacetylation of ethyleneimine/isobutylene block copolymers was effected by alkaline hydrolysis.

A. Synthesis and Characterization of Linear and Three-Arm Star Tosyl-Telechelic Polyisobutylenes.

According to preliminary experiments the tosylation of alcohol-telechelic PIB's in the presence of pyridine or triethylamine gave only ∿ 60% tosylated product even after 48 hours at room temperature. In contrast, quantitative tosylations have been obtained by the use of 4-N,N-dimethylaminopyridine (DMAP). According to Hofle et al. (1978) the catalytic activity of DMAP in acylation is ∿ 10^4 times greater than that of pyridine.

Evidence for quantitative tosylation of alcohol-telechelic PIB's was obtained by IR and ^{1}H-NMR spectroscopy, gel permeation chromatography, and indirectly by obtaining quantitative blocking of 2-Me-2-Oxz from the tosylate-telechelic PIB macroinitiators.

IR spectra of both the linear and the three-arm star tosyl-telechelic PIB's (Figure 1) indicate the complete absence of absorptions at 3645 cm^{-1} characteristic of $-CH_2OH$, however, exhibited absorptions associated with the tosyl group ($\nu_{arom}C = C$, 1594 cm^{-1}), the sulphonate ester group (1170 cm^{-1}) and the aromatic ring in the tosyl group (776-804 cm^{-1}).

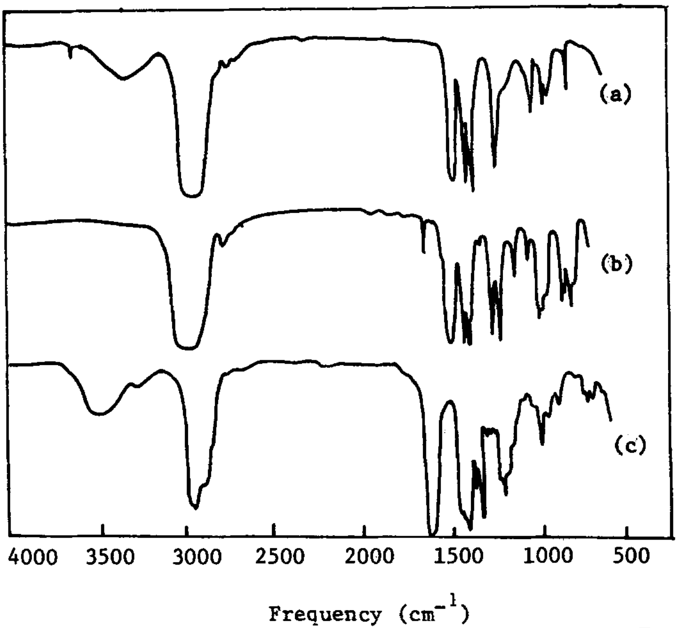
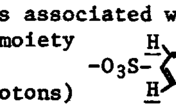
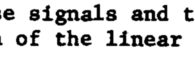


Fig. 1. IR spectra of: α,ω-di(hydroxy)polyisobutylene ($\bar{M}_n$= 4,780)(a); α,ω-di(tosyl)polyisobutylene ($\bar{M}_n$= 3,400) (b); poly(N-acetylethyleneimine-b-isobutylene-b-acetylethyleneimine (Sample 1, Table 2) (c)

Representative proton NMR spectra of a linear starting material, α,ω-di(hydroxy)polyisobutylene, and the products obtained from it, i.e., the tosylate, the N-acetylethyleneimine and the ethyleneimine triblock copolymers, are shown in Figures 2a&d. The resonance at 3.25 ppm characteristic of $-\underline{CH_2}OH$ protons in the starting material is absent in the spectrum of the tosylated product (2b), however, the latter exhibits a resonance at 3.7 ppm characteristic of the methylene protons in the tosylate group $-\underline{CH_2}-O-C_6H_4-CH_3$ (SAEGUSA and IKEDA, 1973; PERCEC, 1981). The resonance (doublet) at 7.2 ppm in Figure 2b is due to the protons ortho to the methyl group of the tosylate moiety  (part of the doublet is masked by the strong resonance at 7.10 ppm due to the four protons of the central aromatic ring of the inifer residue), whereas the doublet at 7.7 ppm is associated with the protons ortho to the sulfonyl group of the tosylate moiety . The singlet at 2.45 ppm is due to the tosyl group. The ratios of the integrated signals at 7.2 ppm (8 protons) and at 7.7 ppm (4 protons), as well as between each of these signals and that at 3.7 ppm (4 protons) indicate quantitative tosylation of the linear alcohol-telechelic PIB. Similar

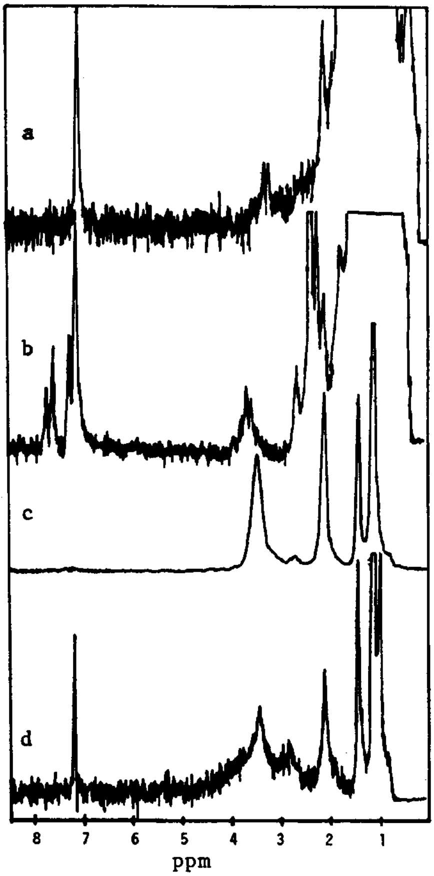


Fig. 2. ^{1}H-NMR spectra of: α,ω-di(hydroxy)polyisobutylene ($\bar{M}_n$= 4,780) (a); α,ω-di(tosyl)polyisobutylene ($\bar{M}_n$= 6,100) (b); poly(N-acetylethyleneimine-b-isobutylene-b-acetylethyleneimine) (Sample 2, Table 2) (c); poly(ethyleneimine-b-isobutylene-b-ethyleneimine) (d)

integration of ^{1}H-NMR spectra of the tri-arm star tosyl-telechelic product also indicated quantitative tosylation.

The uniformity of tosylation, i.e., the tosyl groups are uniformly distributed among all polymers in a sample, has been proven by linear $(UV/RI)_{max}/(UV/RI)_x$ versus $(MW)_x/(MW)_{max}$ plots having slopes close to unity (KENNEDY and SMITH, 1980).

B. Synthesis and Characterization of Linear and Three-Arm Star N-Acetylethyleneimine/Isobutylene Block Copolymers.
Tosyl-telechelic polyisobutylenes have been used as macroinitiators to induce the block copolymerization of 2-Me-2-Oxz. Experimental conditions and results are shown in Table 2. The crude product was first extracted with water to remove poly(N-acetylethyleneimine) homopolymer. The presence of the latter was anticipated because chain transfer to monomer has been proposed to occur in oxazoline polymerization (LITT et al., 1975). According to proton NMR spectroscopy, the water soluble fraction did not contain PIB. Extraction of the water-insoluble fraction with hexanes did not produce soluble material indicating the absence of PIB homopolymer. The water-and-hexane-insoluble fraction is regarded as the target poly(N-acetylethyleneimine-b-isobutylene-b-N-acetylethyleneimine). The absence of even traces of tosylate group in the resulting block copolymers (IR and ^{1}H-NMR) suggests quantitative utilization of the tosylated polyisobutylenes as initiators for the ring opening polymerization of 2-Me-2-Oxz.

IR and ^{1}H-NMR spectroscopy of the water-and-hexanes-insoluble fraction confirm efficient blocking of 2-methyl-2-oxazoline from tosyl-telechelic PIB. IR spectra exhibit the absorptions characteristic of the PIB moiety together with those of the amide group at 1630 cm^{-1} (Figure 1). Similarly ^{1}H-NMR spectra show resonances associated with the $-C\underline{H}_3$ and $-C\underline{H}_2-$ groups (at 1.13 and 1.43 ppm) of PIB and those of the $-COC\underline{H}_3$ and $-N-C\underline{H}_2-C\underline{H}_2-$ groups (at 2.13 and 3.47 ppm) of the N-acetylethyleneimine repeat unit (Figure 2c).

By knowing the $\bar{M}_n$ of the tosyl-telechelic PIB starting material, the overall composition of the block copolymers have been determined by ^{1}H-NMR spectroscopy. Columns 8 and 9 of Table 2 show $\bar{M}_n$'s of the PIB and the poly (N-acetylethyleneimine) blocks. Blocking efficiencies (B_{eff}= 100 $b_w/(b_w+h_w)$

where b_w = weight of 2-Me-2-Oxz blocked from the tosyl-telechelic PIB, and h_w = poly(N-acetylethyleneimine) homopolymer formed shown in the last column of Table 2 are 70-80%. B_{eff}'s are less than 100% likely on account of chain transfer to monomer during 2-Me-2-Oxz polymerization.

The solubility characteristics of linear and tri-arm star block copolymers of N-acetylethyleneimine/isobutylene have been investigated and the results are collected in Table 3. The solubility pattern of the block copolymers seems to follow that of the longer poly(N-acetylethyleneimine) sequence (see Table 1). That the solubility is strongly affected by the relative block lengths is indicated by the reversals (S*) indicated in Table 3.

Table 3. Solubility Properties of 2-Methyl-2-Oxazoline/Isobutylene Block Copolymers at 23°C

Solvent	PIB	Poly(2-Methyl-2-Oxazoline)	Block Copolymers
$CHCl_3$	S	S	S
CH_2Cl_2	S	S	S
CCl_4	S	I	I
CH_3OH	I	S	I(S*)
C_2H_5OH	I	S	I(S*)
$(CH_3)_2CO$	I	S	I(S*)
$(C_2H_5)_2O$	S	I	I
H_2O	I	S	I
THF	S	I	I
DMF,DMSO	I	S	I(S*)
Hexanes	S	I	I
$C_6H_5CH_3$	S	I	I

S = Soluble, I = Insoluble, S* = block copolymer 1 from Table 2 is soluble

The glass transition temperatures of these block copolymers have been determined. DSC traces show two Tg's at +75° and -60°C characteristic of long poly(N-acetylethyleneimine) and PIB segments, respectively, and a crystalline melting point at 150°C ostensibly associated with poly(N-acetylethyleneimine).

C. Acetolysis of Poly(N-acetylethyleneimine-*b*-PIB-*b*-N-acetylethylene imine)

The linear block copolymer 1 in Table 2 has been hydrolyzed under alkaline conditions and the product was characterized by IR and ^1H-NMR spectroscopy. According to IR spectroscopy the intensity of the band associated with the amide group at 1630 cm^{-1} diminished reactive to the starting material and a new relatively weak band due to the presence of NH groups in polyethyleneimine appeared at 3260 cm^{-1}. The ^1H-NMR spectrum (in $CDCl_3$) exhibits a broad signal at 3.47 ppm characteristic of $-\underline{CH_2}-N(COCH_3)-\underline{CH_2}-$ sequence and a new resonance at 2.8 ppm due to protons in the $-\underline{CH_2}-NH-\underline{CH_2}-$ grouping.

The resonance at 2.13 ppm is due to protons in $-\mathrm{COC}\underline{\mathrm{H}}_3$ and $-\mathrm{N}\underline{\mathrm{H}}-$. The addition of D_2O reduces the intensity of the latter resonance with the simultaneous appearance of a signal associated with H_2O. Integration of the resonances at 2.8 and 3.47 ppm suggests 60% acetolysis. Saegusa et al. (1973) also found that alkaline hydrolysis of N-acetylethyleneimine units proceeds only to 60-70%.

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