

Thermoreversible Organogels from Alkane Gelators with One Heteroatom

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We have examined the abilities of five structurally simple molecules to form thermoreversible gels with a variety of organic liquids. Each gelator is an acyclic alkane with one heteroatom. Of these, dioctadecylamine (**2N**) is the most efficient gelator. At ≈ 3 wt % concentrations, it forms gels with alkanes, aromatic liquids, alkanols, methylene chloride, and silicone oil that are stable in closed containers at room temperature for >7 months. Each of the other molecules—octadecylamine (**1N**), trioctadecylamine (**3N**), methyldioctadecylamine (**MeN**), and ditetradecylsulfide (**2S**)—is able to gel at least silicone oil, and **3N** and **2S** also form stable gels with alkanols. The reason for the superiority of **2N** as a gelator has been linked to its rodlike structure and ability to act as both a hydrogen-bond donor and hydrogen-bond acceptor. Evidence for the importance of H-bonding interactions in strands of the gels is found in infrared and differential scanning calorimetric measurements on the gelators in their neat and gelled phases and from comparisons of gelation temperatures. Some of the gels were examined also by polarized optical microscopy. These molecules are structurally among the simplest organogelators discovered to date. The fact that no more than one point of potentially strong interaction can exist between molecules in their assemblies requires a severe modification of current models for the necessary structural attributes of organogelators.

Introduction

Organogels are bicontinuous colloidal systems that coexist as micro-heterogeneous solid (i.e., gelator) and liquid phases. The solid part consists of complex networks of strands that are dispersed throughout the organic liquid component. Since the gelator concentrations are usually <2 wt % and can be much less than 1 wt %, there need be no specific liquid–gelator interactions on the molecular scale; in most cases, the liquid component is immobilized primarily by surface tension. Numerous examples of molecules capable of being effective gelators of at least some organic fluids have appeared in the literature.¹ Most gelators have complex molecular structures, frequently with both hydrophobic and hydrophilic regions and several functional groups, including heteroatoms. A notable exception, partially fluorinated long *n*-alkanes, contains several heteroatoms and must be present in greater than 10 wt % concentrations to effect gelation of some liquids at room temperature.² Recently, we reported that some very simple organic molecules gel a variety of organic liquids in a thermally reversible fashion. For instance, selected quaternary ammonium salts are efficient gelators of some alkanes, alkanols, aromatic liquids, and dimethyl sulfoxide.³ Most recently, we have documented the

properties of gels with the simplest possible class of organogelators, long-chained *n*-alkanes.⁴

Here, we report properties of thermally reversible organogels made from five heteroalkane gelators (Chart 1). Each contains no rings or unsaturated groups and only one heteroatom; three are one atom from being *n*-alkanes! They are structurally among the simplest gelators found to date.

Experimental Section

Instrumentation. Melting points were measured and optical micrographs were recorded on a Leitz 585 SM-LUX-POL microscope equipped with crossed polars, a Leitz 350 heating stage, and an Omega HH21 microprocessor thermometer connected to a J-K-T thermocouple. Gels for optical microscopy were sealed in 0.2 mm flattened capillaries. Thermally induced phase changes of neat and gelled materials were followed using a TA 2910 differential scanning calorimeter (DSC) interfaced to a TA thermal analyst 3100 controller. Samples for DSC analyses were placed in open aluminum pans and were heated under a slow stream of nitrogen at a rate of 5 °C/min; cooling was uncontrolled and depended on the difference between ambient and sample cell temperatures. Infrared spectra were recorded on a Midac FT-IR spectrometer interfaced to a PC using Spectra-Calc software. Gels for IR spectroscopy were sandwiched between AgCl plates separated by Teflon spacers.

Materials. Solvents were reagent grade and used as received. Purities are according to suppliers. Trioctadecylamine

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Chart 1. Molecular Structures of Heteroatom Alkane Gelators

	$R_1R_2R_3N$	$H(CH_2)_{14}S(CH_2)_{14}H$
1N	$R_1 = H(CH_2)_{18}, R_2 = R_3 = H$	2S
2N	$R_1 = R_2 = H(CH_2)_{18}, R_3 = H$	
3N	$R_1 = R_2 = R_3 = H(CH_2)_{18}$	
MeN	$R_1 = R_2 = H(CH_2)_{18}, R_3 = CH_3$	

(3N; mp 54.0–54.9 °C; lit. mp 54.0 °C⁵) was synthesized according to the literature.⁵ Dioctadecylamine (2N; >99%, Fluka; mp 70.1–72.5 °C; lit. mp 72.3 °C⁶), ditetradecylsulfide (2S; TCI; mp 51.7–52.8 °C; lit. mp 51.7–52.0 °C⁷) and methyldioctadecylamine (MeN; 95%, TCI; mp 44.2–47.4 °C; lit. mp 43–45 °C⁸) were used as received. Octadecylamine (1N; 98%; Aldrich; mp 52.3 °C; lit. mp 53.1 °C⁹) contained a considerable amount of octadecylammonium octadecylcarbamate¹⁰ which decomposed at ca. 90 °C (as determined by optical microscopy). Vacuum distillation had little effect on the overall composition of the material as observed by polarized optical microscopy.

Samples for gelation studies were prepared by placing a known amount of solvent with the amine or sulfide in a glass pipet sealed at one end. The other end was flame-sealed and the samples were twice heated until the solid dissolved and cooled to room temperature before making qualitative measurements. Gelation was considered successful if, upon inverting the container after a third heating and undisturbed cooling cycle, no sample flow was observed (i.e., the inverse flow method).¹¹ If part of the sample fell, the sample was classified as a partial gel. Samples that fell entirely were characterized as either a solution or a precipitate, depending on their physical appearance.

The gel transition temperature (T_g) was measured when an inverted solidlike gel, placed in a thermostated water bath, became fluidlike (i.e., fell under the influence of gravity). Ranges of T_g were recorded from the start of sample flow until the entire sample had fallen.

Results

Thermodynamic Properties of Neat Gelators.

Transition temperatures, and their enthalpies and entropies (of reversible transitions) for neat 1N, 2N, 3N, MeN, and 2S are summarized in Table 1. 1N showed two endothermic transitions during the first heating and one exothermic transition upon cooling. The lower and higher temperature transitions during first heating correspond to the melting of octadecylamine and to decomposition of octadecylammonium octadecylcarbamate to octadecylamine and carbon dioxide.¹⁰ The carbamate forms when 1N is exposed to CO₂ in the air.¹⁰ In subsequent scans, run immediately thereafter, the enthalpy of the decomposition transition was lower. Upon cooling, only the freezing transition of octadecylamine was observed. Some carbamate was present in the gels employing 1N. For that reason, only qualitative

conclusions should be drawn from these gels, and the heat associated with the melting transition is a lower limit to the value for a pure sample.

2N displayed only one transition upon heating (melting) and one upon cooling, with very little hysteresis. In subsequent scans, an additional solid–solid transition, a shoulder, was observed upon heating. In all heating and cooling scans of 3N, only one transition was detected; the cooling transition is somewhat complex. 2S exhibits two peaks upon heating and two upon cooling. By optical microscopy, the lower temperature transition is between two solid phases. The appearance of the thermograms of MeN resembles those of 2N, but the transition temperatures and enthalpies are consistently lower.

Qualitative Gelation Tests (Table 2). For comparison purposes, the molar concentration of one gelator was kept constant in samples with different liquids (except for samples in which 3N and MeN did not form a gel). At the same molar concentration, the weight percent of a lower molecular-mass gelator is obviously lower than one with a higher molecular mass. As such, higher molecular-mass species have an intrinsic gelling advantage over lower ones in most of our experiments. Only gels of 2N and 2S were prepared at the same weight percent.

MeN, 2N in which the ability to donate H-bonds is blocked, was the least efficient gelator of the liquids in Table 2. 1-Pentanol was gelled only partially and the other liquids were not gelled at all by 1N. Both 3N and 2S were able to gel only the alcoholic liquids. Gels with 2N formed in all liquids tested and, like those of 3N and 2S, remained stable for >7 months.

Gels of 2S were different in appearance from other turbid gels. Large, platelike, crystalline domains were barely discernible without magnification, but were detectable by optical microscopy; these gels are very heterogeneous. The arrays of flat, platelike 2S crystals are not like the strand assemblies found in most organogels.¹

All of the gelators were able to gel tetramethyltetraphenylsiloxane (Dow silicone oil 704¹²) (Table 3). The two lowest molecular-mass gelators, 2S and 1N, required higher concentrations to effect gelation of this liquid. The T_g values of 2N and 3N are strongly dependent on concentration. The critical gelator concentrations, below which gels do not form at room temperature, are <10 mM for both. In the lower concentration ranges, most gels are transparent or translucent. As concentration is increased, turbidity and T_g increase as well. Consistently, T_g values for 2N are the highest at comparable weight percent concentrations.

Thermodynamic Properties of Gels. 2N, clearly the most efficient gelator, and silicone oil, the least volatile liquid, were selected for careful DSC examinations. The amount of silicone weight loss during DSC scans is negligible and, thus, does not interfere with the calculation of transition enthalpies: after two heating/cooling cycles, no weight loss was found; thermograms of the two cycles are virtually identical. The dependence

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Table 1. Transition Temperatures, Enthalpies (ΔH), and Entropies (ΔS) from DSC Thermograms of Neat Gelators^a

	first cycle						ΔS^c (J/(mol K))
	heating		cooling		second cycle heating		
	T (°C) ^b	ΔH (kJ/mol)	T (°C)	$-\Delta H$ (kJ/mol)	T (°C)	ΔH (kJ/mol)	
1N	49.8 ^d	56.9	46.2	73.3	49.9	72.2	227
	81.7	11.3	<i>e</i>	<i>e</i>	71.5	2.1	<i>e</i>
2N	70.9	134	69.1	121	69.4 ^d	130	366
3N	52.1	148	41.0 ^d	136	49.8	134	424
MeN	46.0	106	32.9	78.0	39.4 ^d	77.2	251
2S	43.2	5.0	34.4	8.9	38.6	5.9	24
	48.4	87.6	47.1	75.4	46.3	81.2	245

^a See text for details. ^b Temperature at the peak onset. ^c ΔS , entropies were calculated from the average ΔH and the average T from the first cooling and second heating thermograms. ^d Includes shoulder peak. ^e Indicates no transition was observed.

Table 2. Gel Transition Temperatures (°C) of Low Molecular Mass Gelators in Various Solvents^a

solvent	1N (concn 0.06 M)	2N (concn 0.05 M)	3N	MeN	2S (concn 0.06 M)
cyclohexane	p (2.0)	31 (3.3)	s (3.7) ^b		s (3.2)
dodecane	p (2.1)	42 (3.4)	s (4.0) ^b	s (4.0) ^b	s (3.3)
hexadecane	p (2.1)	45 (3.3)	p (2.1) ^b		s (3.2)
benzene	p (1.8)	30–33 (2.9)	s (4.0) ^b	s (4.0) ^b	s (2.9)
toluene	p (1.8)	34 (3.0)	s (4.0) ^b		s (2.9)
styrene	p (1.8)	32–36 (2.8)	s (3.3) ^b	s (5.0) ^b	s (2.7)
CH ₂ Cl ₂	p (1.2)	31 (1.9)	s (8.0) ^b		s (1.9)
1-butanol	p (2.0)	45 (3.1)	45 (3.7) ^c		36 (3.1)
1-pentanol	pg 38–52 (2.0)	45 (3.1)	43 (3.7) ^c	s (5.0) ^b	34 (3.1)
1-octanol	p (1.9)	39 (3.1)	38–39 (3.6) ^c		29 (3.0)

^a All gels appeared turbid. Numbers in parentheses are gelator concentrations in wt %. pg is a partial gel. p = precipitate, and s = solution. ^b Molar concentrations vary. ^c The concentration of **3N** in alcoholic liquids is 0.04 M.

Table 3. Gel Transition Temperatures (°C) of Low Molecular Mass Gelators in Tetramethyltetraphenylsiloxane^a

concn (M)	1N	2N	3N	MeN	2S
0.0025			jelly (0.18)		
0.005		jelly (0.24)	Tr (0.36)		
0.01		Tr 40 (0.5)	36 (0.72)		
0.02		47–48 (1.0)	41 (1.4)		
0.04		52 (1.9)	45 (2.8)		p (1.6)
0.06	jelly (1.5)	55–56 (2.9)	48 (4.2)		C 34 (2.3)
0.08	Tu 40 (2.0)	Tu 58 (3.8)	Tu 49 (5.5)	Tu (4.0)	C 36 (3.1)

^a Tr = transparent gel; Tu = turbid gel; jelly = thick solution; C = microcrystallites detectable by the eye; p = precipitate. Numbers in parentheses are gelator concentrations in wt %.

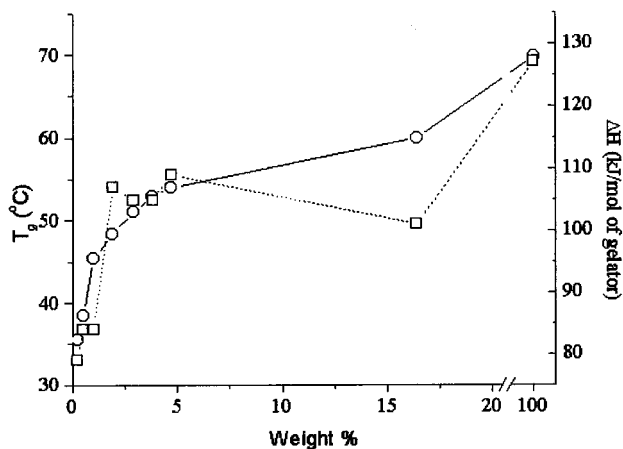


Figure 1. Gel transition temperature (T_g , \circ) and molar transition enthalpies (ΔH , \square) vs weight percent of **2N** in tetramethyltetraphenylsiloxane, from the average of the first heating and cooling DSC scans. T_g was taken as the peak onsets.

of the transition enthalpy and T_g on weight percent of gelator is summarized in Figure 1. T_g data are more precise than those for enthalpies (or entropies) of

transitions since the latter are more sensitive to weighing errors. We estimate that the maximum error in ΔH is $\pm 5\%$, although 3 significant figures are reported in the tables. The transition curves define the boundaries between the gel and the isotropic (or sol) phases. The slopes of both curves are large at low gelator concentrations and plateau at higher ones. Entropies of transitions, calculated from $\Delta H/T = \Delta S$, follow the same trend. This compartment has been observed in many gelator systems. It has been ascribed to the initial filling of the liquid volume by interacting colloids and then, at the higher concentrations, to more extensive branching of the strand networks.¹

Optical Microscopy. The turbidity of gels was dependent on the rate of cooling. Gels composed of relatively low concentrations of gelator (slightly greater than the critical gel concentration) were more transparent if cooled quickly. Figure 2 shows the optical micrographs of 0.02 M **2N**–styrene gels after slow cooling (sol left on the hot stage of the microscope while the block returned to room temperature), moderate cooling (sol cooled in air), and fast cooling (sol immersed in a water bath at 5 °C); the size of solid domains significantly increased as the rate of cooling decreased.

Infrared Spectroscopy. The characteristic weak absorption of the N–H stretching band,¹² 3287 cm⁻¹, was the same for a 0.08 M **2N**–tetramethyltetraphenylsiloxane gel and solid **2N** in KBr. The relatively low frequency indicates intermolecular hydrogen-bonding and the narrowness of the band is consistent with a limited range of orientations between bonding pairs.¹³

Discussion

The greater efficiency of **2N** as a gelator appears to be related to its ability to be both a hydrogen-bond donor

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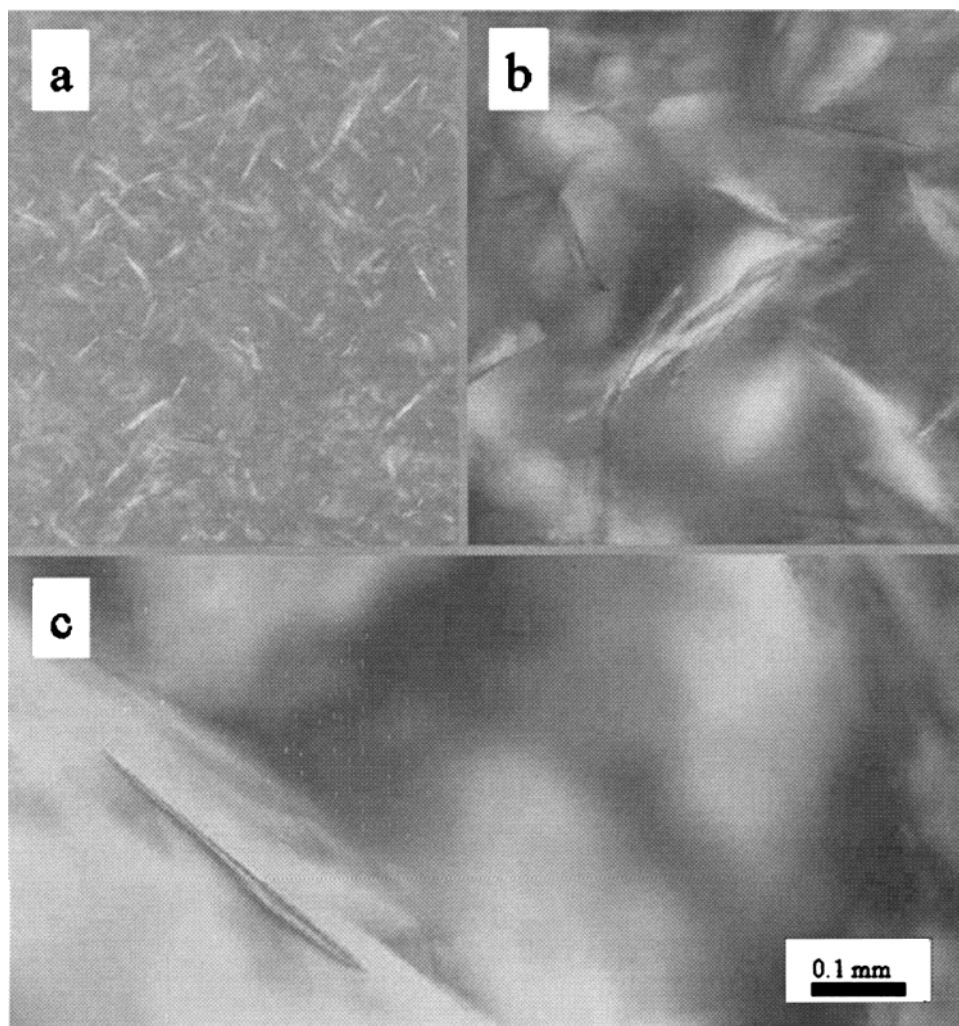


Figure 2. Optical micrographs of a 0.02 M **2N**/styrene gel after (a) fast, (b) moderate, and (c) slow cooling (see text). Each picture was taken at the same magnification.

and acceptor. **2S**, **MeN**, and **3N** can act only as H-bond acceptors. Although **1N** can also act as both a donor and an acceptor, the molecular packing arrangement of its solid may not be amenable to gelation. In addition, the carbamate impurity⁹ may influence the formation of **1N** gels by catalyzing nucleation of morphs that are not amenable to strand formation. **2S**, **2N**, and **MeN** are relatively linear molecules whose heteroatom or heterogroup is in the middle of an alkane chain. Both **2S** and **MeN** are structurally like **2N**, but they cannot donate H-bonds. As a result, stabilization of their neat assemblies cannot rely principally on weaker van der Waals forces. Other work in our lab, with a series of symmetrical tetraalkylammonium salts at the same molar concentration, has demonstrated that T_g and gelation ability are lower when alkyl chains are shorter.¹⁴ Hanabusa et al. have reported a similar trend with trialkyl-*cis*-cyclohexanetricarboxamide gelators.¹⁵ The shorter chain length of **2S** may also contribute to its inefficiency.

Unfortunately, the organization of the gelator molecules in their strands is not known. However, the positions and appearances of the IR absorption bands

for the N–H stretch of **2N** suggest that the same solid morph may be responsible for its bulk solid and the strands in the siloxane gel.¹⁵ We have noted that many organogelators are polymorphous; it is dangerous to assume that molecular organizations in the gelator and bulk solid phases are the same.¹⁶ Since the melting temperature of neat **2N** is the highest of the five gelators examined, its intermolecular interactions may be strongest, at least in the bulk solid phase. On a per chain basis, the enthalpy and entropy of melting of the four amines follow the order **1N** (73 kJ/(mol chain); 227 J/(mol chain K)) > **2N** (60 kJ/(mol chain); 183 J/(mol chain K)) > **3N** (45 kJ/(mol chain); 142 J/(mol chain K)) > **MeN** (39 kJ/(mol chain); 126 J/(mol chain K)). The higher enthalpy and entropy per octadecyl chain for **1N** and **2N** are attributed to strong hydrogen-bonding interactions not possible in the other gelators. This is most apparent when comparing the structurally comparable gelators, **2N** and **MeN**, where the transition enthalpy and entropy of the H-bonding molecule are 55% and 46% greater, respectively, than those of the methylated one.

For all the gelators at equal molar concentrations, T_g decreases as the chain length of the alcohol liquid

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increases. We attribute this trend to the greater solubility of the gelator in the longer alcohols. This trend is also consistent with the greater difficulty experienced by the gelators to gel alkane liquids. **2S**, **MeN**, and **3N** do not precipitate from alkane solutions; they remain solubilized.

There is a good linear relationship between $\ln \chi_g$ and T_g^{-1} for siloxane gels (Figure 3). The data in this form can be analyzed according to the Schröder–van Laar equation (eq 1), assuming (incorrectly) that the gels form ideal solutions on heating.¹⁷ In this equation, χ_g is the mole fraction of gelator and ΔH_{fus} and T_{fus} are the enthalpy of melting of the gel strands and the melting temperature of the neat gelator, respectively. Then, from Figure 3, the calculated melting enthalpy for neat gelator is 137 (intercept) or 139 kJ/mol (slope).

$$\ln \chi_g = \frac{\Delta H_{\text{fus}}}{RT_g} + \frac{\Delta H_{\text{fus}}}{RT_{\text{fus}}} \quad (1)$$

These values are slightly larger than the ΔH from DSC measurements, 134 kJ/mol (Table 1), but all are the same within experimental error. Lower ΔH values from DSC than from the Schröder–van Laar equation have been reported by Shinkai et al.¹⁸ for a very different class of organogels. The excess enthalpy from the gels is probably from the heat of dissolution that accompanies melting of gelator strands.

Conclusions

We have investigated the ability of five structurally simple alkanes that contain only one heteroatom to gel a variety of organic liquids. Optical microscopy, infrared spectroscopy, differential scanning calorimetry, and

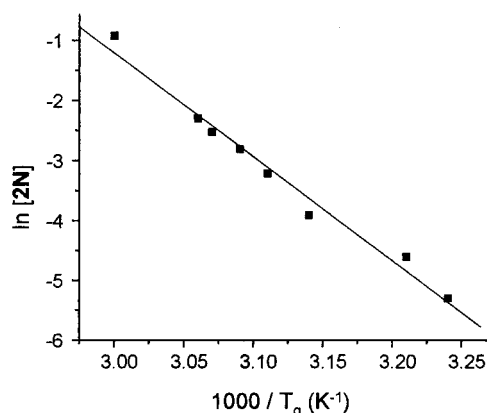


Figure 3. Semilog plot of the molar concentration of **2N** in tetramethyltetraphenylsiloxane vs the inverse of gelation temperature.

measurements of the gelation temperatures have been used to characterize the systems. Of these, **2N** is the most diverse gelator and produces the most stable gels. Infrared spectroscopy confirms that hydrogen bonding is present in the gel strands of **2N**. If intermolecular hydrogen bonding is not possible, as in **2S** or **MeN**, the methylated version of **2N**, the efficiency of gelation is reduced significantly. The additional solubility of **MeN** in the liquids examined also contributes to its inefficiency.

The most important observation from this work is that exceedingly simple low molecular-mass molecules are capable of forming thermoreversible gels with several types of organic liquids. The presence of no more than one point of potentially strong intermolecular interactions (and, in some cases, none) in the molecules reported raises serious challenges to the validity of current models that describe the necessary structural attributes of organogelators.¹ A logical extension of this work, to gel organic liquids with *n*-alkane gelators, has been accomplished.⁴

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