

# Syntheses of Alternating Head-to-Head Copolymers of Vinyl Ketones and Vinyl Ethers, and Their Properties. Ring-Opening Polymerization of 2,3,6-Trisubstituted-3,4-dihydro-2H-pyrans

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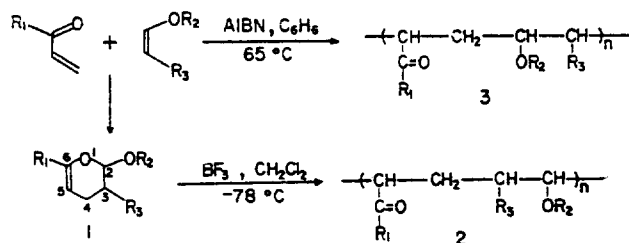
2-Methoxy-6-methyl-3,4-dihydro-2H-pyran (**1<sub>a</sub>**), 2-ethoxy-3,6-dimethyl-3,4-dihydro-2H-pyran (**1<sub>b</sub>**), and 2-ethoxy-3-methyl-6-ethyl-3,4-dihydro-2H-pyran (**1<sub>c</sub>**) were prepared by (4+2) cycloaddition reaction from the corresponding vinyl ketones and alkyl vinyl ethers. Compounds **1<sub>a-c</sub>** were ring-open polymerized by cationic catalyst to obtain alternating head-to-head (H-H) copolymers. For comparison, copolymer of head-to-tail (H-T) was also prepared by free radical copolymerization of the mixture of the corresponding monomers. The H-H copolymer exhibited some differences in its <sup>1</sup>H NMR and IR spectra. However, significant differences were showed between the H-H and H-T copolymers in the <sup>13</sup>C NMR spectra. Also noteworthy was that *T<sub>g</sub>* value of H-H copolymer was higher than that of the corresponding H-T structure. Decomposition temperature of the H-H copolymer was lower than that of the H-T copolymer. All the H-H and H-T copolymers were soluble in common solvents.

## Introduction

In recent years, extensive interest has been focused on the syntheses, characterization, and properties of vinyl polymers having head-to-head (H-H) structure<sup>1</sup>. We have reported recently<sup>2</sup> a novel synthetic route to H-H alternating copolymers by ring-opening polymerization of substituted 3,4-dihydro-2H-pyrans. This work is now extended to the construction of H-H alternating copolymers of another pair of vinyl monomers. The present report describes the syntheses and ring-opening polymerization of 2,3,6-trisubstituted 3,4-dihydro-2H-pyrans which lead to H-H alternating copolymers of vinyl ketones and vinyl ethers. Properties of the resulting H-H copolymer were compared with those of the corresponding head-to-tail (H-T) copolymer.

## Results and Discussion

The cyclic adducts 2-alkoxy-3,6-dialkyl-3,4-dihydro-2H-pyran (**1<sub>a-c</sub>**) were prepared according to a procedure similar to that reported already<sup>3,4</sup> from the corresponding vinyl ketones and vinyl ethers. The chemical structures of the



**1<sub>a</sub>**, **2<sub>a</sub>**, **3<sub>a</sub>**: R<sub>1</sub>=CH<sub>3</sub>, R<sub>2</sub>=CH<sub>3</sub>, R<sub>3</sub>=H

**1<sub>b</sub>**, **2<sub>b</sub>**, **3<sub>b</sub>**: R<sub>1</sub>=CH<sub>3</sub>, R<sub>2</sub>=CH<sub>2</sub>CH<sub>3</sub>, R<sub>3</sub>=CH<sub>3</sub> (no polymer, **3<sub>b</sub>**)

**1<sub>c</sub>**, **2<sub>c</sub>**, **3<sub>c</sub>**: R<sub>1</sub>=CH<sub>2</sub>CH<sub>3</sub>, R<sub>2</sub>=CH<sub>2</sub>CH<sub>3</sub>, R<sub>3</sub>=CH<sub>3</sub> (no polymer, **3<sub>c</sub>**)

Synthetic Scheme

substituted pyrans were identified by <sup>1</sup>H NMR (Figure 1) and IR spectra. Spectral data indicated<sup>7</sup> that **1<sub>b</sub>** and **1<sub>c</sub>** were mixture of the *cis*- and *trans*-isomer. All the spectral evidences confirmed the expected structures.

2,3,6-Trisubstituted pyrans **1<sub>a-c</sub>** were polymerized with cationic catalyst such as boron trifluoride etherate to obtain H-H alternating copolymers **2<sub>a-c</sub>** of vinyl ketones and alkyl vinyl ethers. The results are summarized in Table 1. The values in Table 1 show that the ring-opening polymerizability of 2,3,6-trisubstituted pyrans **1<sub>b-c</sub>** is comparable to that of 2,6-disubstituted pyran **1<sub>a</sub>**, and polymerized well in ring-opening fashion with cationic catalyst at low temperature.

In the cationic ring-opening polymerization shown in Scheme 1 the catalyst initiates the polymerization by attacking a monomer molecule at C<sub>5</sub>, thereby resulting in formation of a cation that rearranges by ring opening to the well known alkoxy cation, which is usually involved in the cationic polymerization of vinyl ethers.

For the purpose of comparison the corresponding H-T

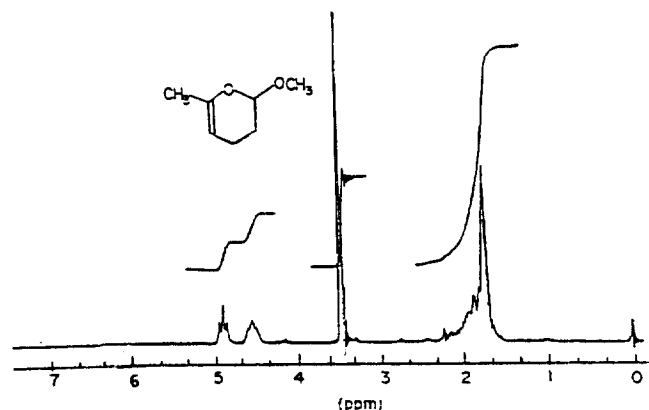
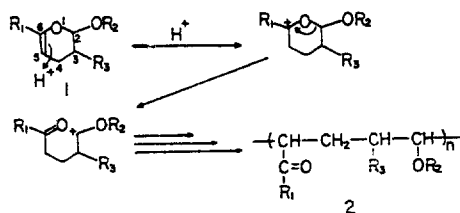


Figure 1. 60 MHz <sup>1</sup>H NMR spectrum of 2-methoxy-6-methyl-3,4-dihydro-2H-pyran (**1<sub>a</sub>**) taken in CDCl<sub>3</sub> at room temperature.

**Table 1. Cationic Ring-Opening Polymerization<sup>a</sup> of 2-Alkoxy-3,6-dialkyl-3,4-dihydro-2H-pyrans **1**... under Various Conditions**

monomer	solvent	monomer solvent (g/ml)	initiator <sup>b</sup> to monomer, mol %	temp, °C	time, hr	% yield	$\eta_{inh}^c$ , dl/g
<b>1<sub>a</sub></b>	CH <sub>2</sub> Cl <sub>2</sub>	0.40	0.7	-78	15	90	0.30
<b>1<sub>a</sub></b>	CHCl <sub>3</sub>	0.35	0.8	-30	12	86	0.27
<b>1<sub>b</sub></b>	CH <sub>2</sub> Cl <sub>2</sub>	0.45	0.9	-78	20	72	0.20
<b>1<sub>b</sub></b>	CHCl <sub>3</sub>	0.50	0.7	-30	36	70	0.18
<b>1<sub>c</sub></b>	CH <sub>2</sub> Cl <sub>2</sub>	0.40	0.8	-78	30	66	0.16
<b>1<sub>c</sub></b>	CHCl <sub>3</sub>	0.50	0.8	-30	48	68	0.15

<sup>a</sup> The copolymer compositions were estimated to the 1.0:1.0 by <sup>1</sup>H NMR spectra. <sup>b</sup> Initiator: Boron trifluoride etherate. <sup>c</sup> Concentration of 0.5 g/dl in chloroform at 20°C.

**Scheme 1**

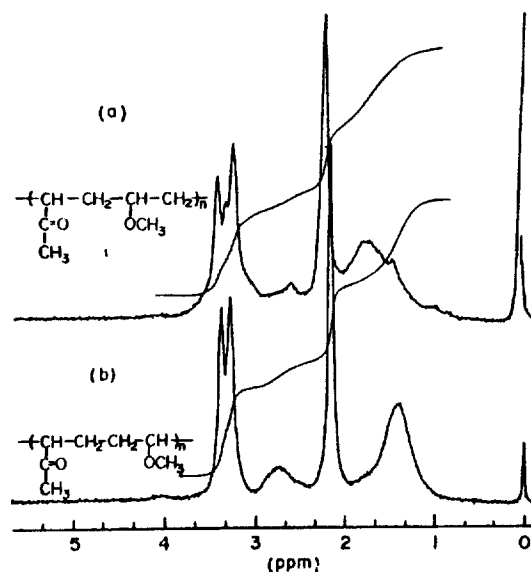
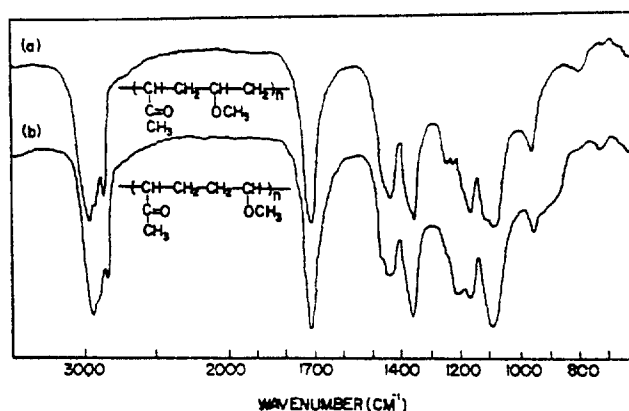
alternating copolymers were prepared by free radical copolymerization of monomeric vinyl ketones and vinyl ethers in benzene with AIBN at 65°C. As expected, this pair of monomers exhibited a high degree of alternating tendency in their radical copolymerization. However, sterically hindered ethyl 1-propenyl ether did not copolymerize with vinyl ketones under the polymerization reaction conditions as shown in Table 2.

Chemical structures of the resulting H-H and H-T copolymers were assigned primarily on the basis of their <sup>1</sup>H NMR and IR spectra. Representative spectra are shown in Figure 2 and Figure 3. However, we failed to observe any significant differences in those of H-H and H-T copolymers. As in the case we have reported before<sup>2</sup>, the decisive spectral difference was observed in their <sup>13</sup>C NMR spectra. Representative <sup>13</sup>C NMR spectra of H-H and H-T copolymers are shown in Figure 4. Assignments of the signals were made on the basis of predicted chemical shifts<sup>5</sup>. As expected, the most

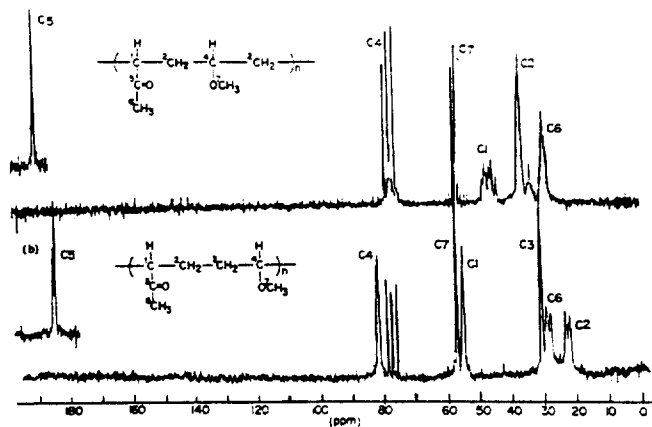
**Table 2. Free Radical Copolymerization<sup>a</sup> of Alkyl Vinyl Ketones with Alkyl Vinyl Ethers by AIBN in Benzene at 65°C**

monomer <sup>a</sup>		A/B, mol	AIBN, mol %	(A+B)/benzene, g/ml	temp, °C	time, hr	yield <sup>c</sup> of product polymer, %	$\eta_{inh}^d$ , dl/g
A	B							
MVK	MVE	0.30	0.70	4.0	65	15	72	0.40
MVK	MVE	0.33	0.75	neat	65	18	66	0.42
MVK	EPE	0.30	0.80	4.0	65	12	80 <sup>e</sup>	0.36
MVK	EPE	0.33	0.70	neat	65	10	84 <sup>e</sup>	0.32
EVK	EPE	0.40	0.80	3.0	65	10	83 <sup>f</sup>	0.34
EVK	EPE	0.33	0.70	neat	65	12	86 <sup>f</sup>	0.31

<sup>a</sup> The copolymer compositions were estimated to the 1.0:1.0 by <sup>1</sup>H NMR spectra. <sup>b</sup> MVK = methyl vinyl ketone; MVE = methyl vinyl ether; EVK = ethyl vinyl ketone; EPE = ethyl 1-propenyl ether. <sup>c</sup> Yields of copolymers were calculated with respect to the comonomer present in smaller molar amount. <sup>d</sup> Inherent viscosity of copolymer: concentration of 0.5 g/dl in chloroform at 20°C. <sup>e</sup> Homopolymer of methyl vinyl ketone was formed. <sup>f</sup> Homopolymer of ethyl vinyl ketone was formed.

**Figure 2.** <sup>1</sup>H NMR spectra of 1:1 alternating copolymers of methyl vinyl ketone and methyl vinyl ether: (a) head-to-tail; (b) head-to-head, 60 MHz, room temperature, arbitrary concentration in CDCl<sub>3</sub>.**Figure 3.** IR spectra of 1:1 alternating copolymers of methyl vinyl ketone and methyl vinyl ether: (a) head-to-tail; (b) head-to-head.

significant difference between <sup>13</sup>C NMR spectra of H-H copolymer (**2<sub>a</sub>**) and H-T copolymer (**3<sub>a</sub>**) is that H-T copolymer exhibited only one signal corresponding to backbone methy-



**Figure 4.**  $^{13}\text{C}$  NMR spectra of 1:1 alternating copolymers of methyl vinyl ketone and methyl vinyl ether: (a) head-to-tail; (b) head-to-head. 20 MHz, room temperature, arbitrary concentration in  $\text{CDCl}_3$ . Chemical shifts are referenced to  $\text{CDCl}_3$  ( $\delta$  77.0) and C-5 signals are swept 20 ppm offset.

**Table 3. Thermal Properties of H-H and H-T Alternating Copolymers of Vinyl Ketones and Vinyl Ethers**

copolymer	type	$T_g$ , $^{\circ}\text{C}$	degradation temp., $^{\circ}\text{C}$		residue <sup>b</sup> at 500 $^{\circ}\text{C}$ , %
			initial	half-loss	
2 <sub>a</sub>	H-H	9	310	385	2.8
3 <sub>a</sub>	H-T	1	345	411	4.3

<sup>a</sup> Determined from DSC curves measured on a 910 differential scanning calorimeter (DuPont Instrument, 990 thermal analyzer) with a heating rate of  $10^{\circ}\text{C}/\text{min}$  in a nitrogen atmosphere. <sup>b</sup> Determined from TGA curves measured in a Perkin-Elmer TGS-1 thermobalance with a heating rate of  $10^{\circ}\text{C}/\text{min}$  in a nitrogen atmosphere.

lene carbon (C-2 in the Figure 4). Furthermore, the signals of C-2 and C-3 of H-H copolymer are shifted toward the higher field than those of C-2 of H-T copolymer, while those of C-1 and C-4 of H-H copolymer are shifted to lower field compared with those of C-1 and C-4 of H-T copolymer.

Another notable aspect is that the resonance peaks of the H-H copolymer reveals the unusual splitting patterns as shown in Figure 4. These spectral evidence seems to indicate that the H-H copolymers are mixtures of several stereoisomers.

All of the copolymers of H-H and H-T structures were soluble in common solvents and reprecipitated from acetone into water. The thermal behavior of H-H and H-T copolymers was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC). The results are summarized in Table 3.  $T_g$  value of H-H copolymer was found to be higher than those of the corresponding H-T polymer, probably due to the chain stiffening by crowded 1,2-disubstitutions. The steric repulsion is further reflected by the lower thermal stability of H-H copolymer compared with conventional H-T copolymer.

We are exploring, further, the polymerization of other substituted pyrans and the results will be reported later.

## Experimental

**Materials.** The reagent grade chemicals were purified by

distillation before use. Methyl vinyl ketone and ethyl vinyl ketone were dried with anhydrous calcium chloride, followed by distillation under reduced pressure. Ethyl 1-propenyl ether was dried over sodium metal, followed by distillation under vacuum. Methyl vinyl ether was prepared by the vinyl *trans*-etherification<sup>6</sup> of *n*-butyl vinyl ether with methanol in the presence of mercuric acetate. Benzene was refluxed over sodium metal, distilled, and stored over molecular sieves under nitrogen. Chloroform was washed with water to remove the ethanol and refluxed with phosphorus pentoxide, followed by fractional distillation. Methylene chloride was dried with anhydrous calcium chloride, distilled over anhydrous calcium sulfate, and stored in a brown bottle with molecular sieves. Boron trifluoride etherate was treated with a small amount of diethyl ether and distilled under reduced pressure.

**Measurements.** All measured temperature was uncorrected. IR spectra were taken on a Perkin-Elmer Model 283B spectrophotometer.  $^1\text{H}$  NMR spectra were obtained on a Varian Model T-60A spectrometer (60 MHz).  $^{13}\text{C}$  NMR spectra were obtained on a Varian FT 80-a NMR spectrometer at room temperature. The glass transition temperatures ( $T_g$ ) were measured on a 910 differential scanning calorimeter (DuPont instrument, 990 thermal analyzer) in a nitrogen atmosphere. A Perkin-Elmer TGS-1 thermobalance with a heating rate of  $10^{\circ}\text{C}/\text{min}$  up to  $500^{\circ}\text{C}$  was used for the thermal degradation study of the polymers in a nitrogen atmosphere.

**Preparation of 2-Methoxy-6-methyl-3,4-dihydro-2H-pyran (1<sub>a</sub>).** Methyl vinyl ketone (35.0 g, 0.50 mol), 34.8 g (0.60 mol) of methyl vinyl ether, and 0.2 g of hydroquinone were placed in a stainless steel bomb. The bomb was cooled and opened. The reddish product was distilled fractionally under vacuum to give 30.7 g (48% yield) of **1<sub>a</sub>**: bp  $54\text{--}56^{\circ}\text{C}$  (20 mm);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.66–2.15 (4H, m), 1.70 (3H, s), 3.45 (3H, s), 4.45 (1H, m), 4.90 (1H, t); IR (neat)  $1690$  ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ .

**Preparation of 2-Ethoxy-3,6-dimethyl-3,4-dihydro-2H-pyran (1<sub>b</sub>).** Methyl vinyl ketone (21.3 g, 0.30 mol), 43.1 g (0.5 mol) of ethyl 1-propenyl ether, and 0.2 g of hydroquinone were placed in a stainless steel bomb. The bomb was then placed in an oven kept at  $150^{\circ}\text{C}$ . After 15 hours the bomb was cooled and opened. Fractional distillation of the product under vacuum gave 24.5 g (52% yield) of **1<sub>b</sub>**: bp  $48\text{--}50^{\circ}\text{C}$  (10 mm);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.80–1.33 (6H, m), 1.60–2.42 (6H, m), 3.32–4.02 (2H, m), 4.33–4.55 (1H, m), 4.55–4.80 (1H, m); IR (neat)  $1690$  ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ .

**Preparation of 2-Ethoxy-3-methyl-6-ethyl-3,4-dihydro-2H-pyran (1<sub>c</sub>).** Ethyl vinyl ketone (16.8 g, 0.20 mol), 25.8 g (0.30 mol) of ethyl 1-propenyl ether, and 0.1 g of hydroquinone were placed in a bomb. The bomb was then placed in an oven kept at  $150^{\circ}\text{C}$ . After 14 hours the bomb was opened, and the resulting reddish product was distilled fractionally under vacuum to give 15.0 g (44% yield) of **1<sub>c</sub>**: bp  $60\text{--}62^{\circ}\text{C}$  (10 mm);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.80–1.32 (9H, m), 1.33–2.65 (5H, m), 3.32–4.10 (2H, m), 4.33–4.55 (1H, m), 4.55–4.80 (1H, m); IR (neat)  $1690$  ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ .

**Cationic Polymerization of 2,3,6-Trisubstituted-3,4-dihydro-2H-pyrans 1<sub>a-c</sub>.** A representative cationic polymerization procedure (the case of **1<sub>a</sub>**) was as follows: A solution of **1<sub>a</sub>** (1.56 g, 10 mmol) in 3.5 ml of purified methylene chloride was introduced into a rubber septum stopper capped glass ampule. The resulting solution was flushed with dry

nitrogen for 20 min. The ampule was then placed in a dry ice-acetone bath under nitrogen and 0.01 ml of boron trifluoride etherate was added to the solution. After 20 hours the polymerization mixture was poured into a large volume of water. The precipitated polymer was collected and reprecipitated from acetone into water. Thus obtained polymer was then dried in a vacuum oven at 40°C. **2<sub>b</sub>**: 1.12 g (72% yield);  $\eta_{inh} = 0.20$  dl/g (c 0.5 g/dl in chloroform at 20°C).

**Preparation of H-T Alternating Copolymer 3<sub>a</sub>**. A representative procedure was as follows: In a pyrex glass ampule were placed 1.40 g (20 mmol) of methyl vinyl ketone, 3.83 g (67 mmol) of methyl vinyl ether, 0.046 g of AIBN, and 1.3 ml of benzene. The ampule was then placed in a dry ice-acetone bath and evacuated. The ampule was sealed under vacuum and placed in an oil bath kept at 65°C. After 15 hours the ampule was opened and excess methyl vinyl ether and benzene solvent was removed by rotary evaporator. The resulting viscous polymer was dissolved in acetone and then poured into a large volume of water. The precipitated polymer was collected and reprecipitated two times from acetone into water. Thus obtained polymer was then dried in a vacuum oven at 40°C. **3<sub>a</sub>**: 1.84 g (72% yield);  $\eta_{inh} = 0.40$  dl/g (c 0.5 g/dl in chloroform at 20°C). The <sup>1</sup>H NMR spectrum of **3<sub>a</sub>** indicated that the composition of the polymer was approximately 1.0:1.0. **Acknowledgements**. The authors wish to thank the Korea Science and Engineering Foundation for partial support of this work.

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7. The resonance peaks of the proton H<sup>3</sup> (**1<sub>b</sub>**) and H<sup>2</sup> (**1<sub>c</sub>**) are splitted into multiplet, while that of **1<sub>a</sub>** is triplet in their <sup>1</sup>H NMR spectra. These spectral data indicate that **1<sub>b</sub>** and **1<sub>c</sub>** are mixtures of *cis*- and *trans*-isomer. Similar stereoisomerism was observed in the other substituted pyrans such as 2,6-diethoxy-3-methyl-5-cyano-3,4-dihydro-2H-pyran and 2-ethoxy-6-methoxy-3-methyl-5-cyano-3,4-dihydro-2H-pyran (ref. 2(e)).

## Study of Vibrational Dephasing of Simple Molecules in Liquids

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A theory in which the Enskog hard sphere collisional dynamics complements the hydrodynamic theory is applied to the fast modulation dephasing dynamics in liquids which leads to homogeneous line broadening in the isotropic Raman spectra. The dephasing times of several molecules in pure liquids and in trace solutions in the solvent CCl<sub>4</sub> are calculated and these are compared with experimental values. The temperature dependence of the dephasing time of liquid acetonitrile and the isothermal density dependence of the dephasing time of liquid methyl iodide are also investigated.

### Introduction

The dephasing of molecular vibrations in liquids has been studied for many years experimentally and theoretically as a probe of molecular interactions and dynamics in liquids<sup>1</sup>. The dephasing phenomena can be experimentally investigated by the isotropic Raman line shape and the picosecond coherent anti-Stokes Raman spectroscopy in the frequency and time domains, respectively. Several theoretical and experimental studies<sup>2-11</sup> have shown that the isotropic Raman line shape provides a direct and useful probe of only the vibrational pure dephasing among various physical mechanisms. The isotropic Raman line shapes are recently known to be significantly inhomogeneously broadened even in nonpolar or non-hydrogen

bonded liquids<sup>12</sup>. In such cases, picosecond coherent Raman experiments can be used to study the homogeneous vibrational dephasing dynamics in inhomogeneously broadened vibrational line shapes<sup>13</sup>.

The physical processes in weak coupling regime which give rise to the vibrational pure dephasing can be divided into fast and slow modulation processes according to their time scales. The fast modulation process gives rise to the homogeneous broadening in isotropic Raman spectra and the slow modulation process causes the inhomogeneous line broadening.

A number of theoretical models have been proposed to explain dephasing phenomena. Among several models for the vibrational dephasing in the fast modulation process, the isolated binary collision model proposed by Fischer and