

Use of low molecular weight oligomers as non-volatile reaction media

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Very low molecular weight oligomers were prepared and evaluated as non-volatile reaction media. This paper reports the results of a preliminary feasibility study on the potential for oligomers to function as environmentally benign and cost-effective replacements for liquid solvents. The preparation and solvent efficacy are reported on two series of low molecular weight vinylpyrrolidone (VP) rich co-oligomers. The first series of oligomers employed 1-hexene as a 'soft' co-monomer, while the second series employed ethyl vinyl ether (EVE) as a 'soft' co-monomer. The 'soft' co-monomer was required to lower the T_g and T_m of the low molecular weight VP-rich oligomer so that a low viscosity liquid could be obtained at suitable reaction temperatures. This study determined the required amount of soft co-monomer and then evaluated the ability of the oligomers to solvate a variety of reactants. Selected oligomers from each series were employed as reaction media in aliphatic and aromatic nucleophilic substitutions, and in condensation reactions. Product yields were compared for both oligomers and for *N*-methylpyrrolidone (NMP), which is structurally similar to the VP repeat unit, and was used as a control solvent. Yields in oligomer solvents were similar to those obtained in NMP. Products were separated from the oligomers by distillation or aqueous extraction. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The volatility of conventional solvents causes them to be susceptible to emissions through stacks and joints (fugitive emissions). Fugitive emissions account for as much as 70% of volatile emissions during chemical production¹. Chemical industries report that 1 billion pounds of TRI-listed chemicals are released directly to the atmosphere annually². Conventional solvents can also be problematic if spilled during shipping because volatile liquids evaporate into the air, penetrate the ground, are easily ignited by sparks, can be inhaled, or irritate skin and eyes. Clean-up of such spills can be difficult and labour intensive.

Use of oligomers as reaction media could significantly reduce atmospheric emissions, and so offer significant environmental, health and safety advantages over conventional solvents. Oligomers have not been studied before as reaction media, therefore, this initial feasibility study was undertaken to demonstrate the potential for oligomers to function as reaction solvents. To accomplish that objective this first study focused on development of an oligomer similar to the polar aprotic solvent, NMP. NMP is not a TRI-listed solvent and is not volatile, but was selected as a model for an oligomeric solvent because of its versatility. NMP can be employed in a variety of reaction types including aliphatic and aromatic nucleophilic substitutions, condensation reactions, and in step-growth polymerizations. Step-growth polymerizations must proceed to more than 99% completion before high-molecular-weight polymer is obtained. Preparation of a high-molecular-weight product in an NMP-like oligomer would demonstrate that the

oligomer solvent properties and mass transfer ability are similar to that of the low molecular weight parent solvent, NMP. Therefore, low-melting, VP-rich co-oligomers were prepared in which the major repeat unit was VP, which is structurally nearly identical to NMP (*Figure 1*). A small amount of a 'soft' co-monomer, 1-hexene or EVE, was incorporated to provide an oligomer with a low T_g and little or no crystallinity.

EXPERIMENTAL

Materials

NMP, VP, ethyl vinyl ether (EVE), and 1-hexene were distilled prior to use. Methylene chloride was distilled twice prior to use. AIBN was purchased from Sigma and purified by recrystallization. All other reagents were purchased from Aldrich Chemical Company or Chriskev Company, Inc., and used as received.

Instrumentation

¹H n.m.r. spectra and FT-i.r. were obtained with a Varian XL 300 n.m.r. and a Nicolet 7199, respectively. Thermal analyses were done with a Shimadzu TGA 50. Size exclusion chromatography (SEC) was done on a Perkin-Elmer 601 equipped with Phenomenex columns and a u.v.-vis detector. Rheological measurements were made with a Bohlin VOR Rheometer system.

Synthesis of VP/1-hexene co-oligomers by a non-living radical method

Low-molecular-weight VP/1-hexene co-oligomers were prepared by simultaneously adding the monomers to toluene in a 1:1 ratio using AIBN initiator and reacting at 80°C under

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a nitrogen atmosphere. In some instances 1-dodecanethiol was employed as a chain transfer agent (CTA). The reaction was allowed to proceed overnight. Monomer concentration, monomer/initiator ratio, and CTA concentration were varied to yield oligomers of different molecular weight, co-monomer content, and CTA content (~50–60% yield). The average co-monomer content was estimated by ^1H n.m.r., but the sequence distribution was not analysed.

Synthesis of VP/EVE co-oligomers by a pseudo-living cationic method

A VP/EVE co-oligomer was prepared by pseudo-living cationic polymerization in methylene chloride at -30°C using boron trifluoride diethyl etherate as the initiator³. The EVE co-monomer was added (33 mol%) by sequential monomer addition over 0.5 h to yield EVE theoretically dispersed within the chain in a non-repeating sequence. The reaction was allowed to proceed 5 h and then quenched with methanol. The co-oligomer was collected by removal of the solvent under reduced pressure (46% yield). The average co-monomer content was estimated by ^1H n.m.r. and found to be 40% EVE. The sequence distribution was not analysed.

Reagent solubility studies in co-oligomers

Co-oligomers (2.0 g) were heated to ~ 100 – 150°C . Selected reagents (0.4 g) were added to the warm oligomer with stirring and heated until a clear solution was obtained or to a maximum of 200°C . The mixture was then allowed to cool to room temperature. The reagent was designated as soluble if a clear liquid or solid solution was retained at room temperature.

Measurement of co-monomer content in co-oligomers

^1H n.m.r. of the monomers, the CTA, and AIBN were run to determine the band position of distinguishable protons. Homo-oligomer spectra were employed to confirm band identity after reaction. Spectra of the co-oligomeric products were obtained in CDCl_3 . The spectra were complex with multiple bands overlapping at most positions. The ratio of protons which were characteristic for each species was determined. By combining SEC results to estimate the number of end-groups to allow the protons from AIBN and CTA could be subtracted from appropriate bands an estimate was made of the relative ratios of the two monomers and monomers to CTA in the oligomers. In most instances the two values agreed within 10%. The single largest difference was 18%. Reported values are the average of the values obtained by the two analytical methods.

Measurement of oligomer molecular weight and polydispersity

Co-oligomers selected for use as reaction media were characterized for molecular weight by size exclusion chromatography (SEC). Solutions were prepared in THF

(10 mg/l) and run through Phenomenex columns packed with $0.5\ \mu$ Phenogel.

Rheological measurements

Co-oligomers selected for use as reaction media were characterized for rheology with a Cone and Plate rheometer (Bohlin VOR Rheometer System) at 150 or 80°C .

Low-molecular-weight condensation reactions in co-oligomers

Model amides were prepared by adding equimolar amounts of benzoic acid and *n*-butylamine, or caproic acid and aniline, with a catalytic amount of *p*-toluenesulfonic acid to the oligomer (50% w/w). The reaction was stirred at 125°C for 3 h. Products were collected by distillation of unreacted material followed by aqueous extraction of the oligomer from non-volatile products. Products were isolated in yields of 52–100%. Control syntheses were done in NMP where the NMP was removed by distillation.

Model imides were prepared by simultaneously adding 2 equivalents of a monofunctional amine to 2 equivalents of a dianhydride (2:1 mol/mol) to oligomer (20% w/w) in a 50 ml round-bottom flask equipped with a reflux condenser, mechanical stirrer, and nitrogen inlet/outlet. A catalytic amount of isoquinoline was added. The reaction was heated in an oil bath for 2 h at 180°C under a nitrogen purge. The reaction was allowed to cool to room temperature and an ethanol–water mixture was added to precipitate the product, which was then collected by filtration. The oligomer was recovered from the filtrate by removal of the solvent under reduced pressure. Product yields were quantitative (^1H n.m.r.) and isolated in 81–100% yield. Products from oligomer and NMP were compared by FT-i.r. and ^1H n.m.r. and found to be identical. No oligomer contamination was found in the product based on n.m.r. analysis.

Condensation polymerizations in co-oligomers

Polyimides were prepared by adding equimolar amounts of diamines and dianhydrides along with a catalytic amount of isoquinoline to oligomer in a 50 ml reaction flask equipped with a reflux condenser, mechanical stirrer, and a nitrogen inlet/outlet. The reaction was heated at 180°C for 2 h in an oil bath under a nitrogen purge. After 2 h the reaction was allowed to cool, ethanol was added and the oligomer/polyimide mixture was stirred at reflux for 2 h, then allowed to cool to room temperature. The solid product was collected by filtration. The extraction was repeated once and the solid product was dried. Isolated product yields ranged from 92 to 99%. Control syntheses were done under the same conditions in NMP except the solvent was removed by distillation.

Aromatic nucleophilic substitution in co-oligomer

Equimolar amounts of *p*-chloronitrobenzene and potassium methoxide were added to the oligomer (20% w/w). The solution was heated at 100°C for 2 h. The product was collected by removal of volatiles under reduced pressure followed by aqueous extraction of the oligomer to give 44–60% yield of product. Oligomer was recovered quantitatively. Separation of by-product was not attempted. Control syntheses were done in NMP under the same conditions.

Aliphatic nucleophilic substitution in co-oligomer

Equimolar amounts of *n*-bromobutane and sodium iodide were added to the oligomer (~50% w/w) and the solution was heated at 100°C for 2 h. Volatiles were collected by

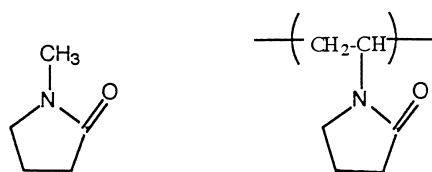


Figure 1 Structure of NMP and of the major repeat unit in the NMP co-oligomer solvents

Table 1 Effect on physical properties of varying initiator concentration

No.	AIBN (mol%)	Monomer (wt%)	CTA (mol%)	Physical state of product	LT (°C)	VP in product ^a (mol%)
1	1.25	40.3	0	Solid	150	79
2	1.50	40.3	0	Solid	165	75
9	1.25	24.2	15.0	Semi-solid	102	59
16	0.5	24.2	15.0	Liquid	—	44

^aObtained from ¹H n.m.r.**Table 2** Effect on physical properties of varying chain-transfer agent

No.	AIBN (mol%)	Monomer (wt%)	CTA (mol%)	Physical state of product	LT (°C)	VP in product ^a (mol%)
1	1.25	40.3	0	Solid	150	79
4	1.25	40.3	2.5	Solid	120	78
5	1.25	40.3	7.5	Semi-solid	120 ^b	74
6	1.25	40.3	12.4	Semi-solid	22 ^c	63
7	1.25	40.3	15.5	Semi-solid		58
8	1.25	40.3	15.5	Semi-solid		60
12	0.5	10.1	15.0	Liquid		49
13	0.5	10.1	12.5	Liquid		63
14	0.5	10.1	10.0	Liquid		61
15	0.5	10.1	7.5	Liquid		47

^aObtained from ¹H n.m.r.^bThe synthesis procedure was refined to give a liquid product with similar VP content^cYielded a viscous melt prior to water-like melt

fractional distillation. Control syntheses were done in NMP under the same conditions; yield: 29–60%.

RESULTS AND DISCUSSION

Synthesis of VP/1-hexene co-oligomers

A series of VP-rich co-oligomers was prepared by conventional radical polymerization methods using AIBN as the initiator (Tables 1–3). Co-oligomers were prepared because even low-molecular-weight VP homo-oligomers were semicrystalline, high melting solids. 1-Hexene was selected as the co-monomer because it is highly plasticizing, so it was anticipated that little would be required to produce amorphous or low melting VP-rich co-oligomers. Initially, no CTA was employed (**1** and **2**). However, these co-oligomers were also high melting, so additional VP/1-hexene co-oligomers were prepared with CTA (**3**–**14**). The comonomer feed ratio was kept constant (1:1) but the amount of CTA, initiator, and overall monomer concentration in toluene, were varied to vary the molecular weight and 'soft' comonomer in the product. The co-oligomers were analysed by ¹H n.m.r. (to determine the average co-monomer and CTA in the oligomer product, but not sequence distribution), and a visual determination was made of the liquefaction temperature (LT) which was the temperature at which all the material was liquid and appeared near water-like. Because the initiator, CTA, and monomer bands had significant overlap two analytical approaches were employed to estimate the average amount of 1-hexene incorporated into the oligomers. In all but three instances the results from the two methods agreed within 10%. The largest difference was 18%. The values obtained by the two methods were averaged and that average reported

Table 3 Effect on physical properties of varying solids concentration

No.	AIBN (mol%)	Monomer (wt%)	CTA (mol%)	Physical state of product	LT (°C)	VP in product ^a (mol%)
1	1.25	40.3	0	Solid	150	79
3	1.25	10.1	0	Solid	105 ^b	83
9	1.25	24.2	15.0	Semi-solid	102	59
10	1.25	15.1	15.0	Semi-solid	80	70
11	1.25	10.1	15.0	Liquid		52

^aObtained from ¹H n.m.r.^bYielded a viscous melt^cYielded a non-viscous, water-like melt**Table 4** Solubility of VP/1-hexene co-oligomers in selected solvents^a

Oligomer	NMP	H ₂ O	Ethanol	Acetone	CHCl ₃	Hexane
1	s	p	s*	s*	s	n
2	s	p	s*	s*	s	n
3	s	p	s*	s*	s	n
4	s	s	s	s	s	n
5	s	p	s	s	s	n
6	s	p	s	s	s	n
7	s	p	s	s	s	n
8	s	p	s	s	s	n
9	s	p	s	s	s	n
10	s	p	s	s	s	n
11	s	n	s	s	s	n
12	s	n	s	s	s	n
13	s	n	s	s	s	n
14	s	n	s	s	s	n
15	s	n	s	s	s	n
16	s	p	s	s	s	n

^aData obtained by adding 0.3 g of oligomer to 2.0 ml of solvent and shaking at room temperature

s = soluble; s* = solution with residual insoluble material; p = opaque but no solid present; n = insoluble

for the VP content in the co-oligomer. By this approach it was found that the oligomer can contain no more than about 65–75% of VP before the melting temperature becomes excessive for a reaction medium.

The formulation which produced **5** was repeated. Procedural refinements reproducibly gave a liquid product. The modified synthesis involved adding initiator and monomer simultaneously over a 20 min period to the preheated solvent (80°C). The solution was then heated to 100°C for 5 h. The liquid product had ~70% VP content by ¹H n.m.r. This procedural modification presumably resulted in reducing the high-molecular-weight fraction of the oligomer.

Characterization of the VP/1-hexene co-oligomers

The co-oligomers were characterized for solubility in water and common organic solvents. Unlike pure PVP, the co-oligomers were not water-soluble, however, several were miscible with water (Table 4). True water-solubility was desired for the co-oligomers so that they could be used as reaction media to prepare products which cannot be collected by distillation. For such separations to be environmentally benign either the product or the oligomer must be able to be separated by aqueous extraction. The results of the solubility study of the co-oligomers in common organic solvents revealed that, as expected with non-living polymerization methods, some homo-oligomer fractions, or fractions very rich in 1-hexene co-monomer, were obtained. This was evident for oligomers **1**–**3**, where clear solutions were obtained in both ethanol and acetone, and residual solid material, presumably a 1-hexene rich

Table 5 Solubility (25% w/w oligomer) of reactants in VP/1-hexene oligomers

Oligomer reactant	5	6	7	8	9
BTDA	s	s ^a	s ^c	n ^d	n ^d
ODPA	s ^c	s ^c	s ^c	n ^d	n ^d
TPE-R	s ^a	s ^a	s ^c	s ^c	n ^d
AA	s ^a	AA	n ^d	n ^d	n ^d
(<i>m,p</i>)-PD	s	p ^b	p ^b	n ^d	n ^d
An	s	s	s	s	s
CMA	s	s	s	s	s
<i>n</i> -Octanol	s	s	s	s	s
CA	s	s	s	s	s
FDA	s ^c	s ^c	s ^c	s ^c	s ^c

^aA slight opacity was observed^bMost of the monomer appeared to dissolve, but some oil was observed^cA clear gel-like solution was obtained at 170°C, a clear melt was obtained at 200°C^dPhase separation^eViscous solution obtained at 175°C**Table 6** Low molecular weight syntheses in oligomer 5

Reaction type	Reactants	% Yield (isolated)	% Yield (control) ^a	Oligomer recovery (%)
ArSn	<i>p</i> -CNB/K-MeO	44	69	
Sn ₂	BrBu/NaI	29	35	
Condensation	BuNH ₂ /BzA	51	69	100
	Me-An/BTDA	100	100	99
	Me-An/ODPA	98	100	98

^aReaction done in NMP as a control and product isolated by removal of NMP by distillation

fraction, remained unsolvated. The oligomers, except for 4, were not truly soluble in water, but were miscible. The water phase appeared hazy, but no undispersed solid matter was visible in the water except in the case of oligomers 1–3.

Oligomers 5–9 were evaluated as solvents for potential reactants (Table 5). The reagents were 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic dianhydride (ODPA), 1,3-bis(4-aminophenoxy)benzene (TPE-R), 9,9-bis(4-aminophenyl)fluorene (FDA) adipic acid (AA), 2-chloro-4-methoxyaniline (CMA), *m*- and *p*-phenylenediamine (*m,p*-PD), aniline (An), and caproic acid (CA). Oligomer 5 was the most effective solvent, could be dispersed in water, and visually had a reasonable melt viscosity, so it was selected for further investigation.

The thermal stability of all the oligomers was less than anticipated. Most began to show weight loss at ~180°C and had 5% weight loss in nitrogen at ~225 ± 10°C. However, 5 was somewhat more stable and had only 5% weight loss at 256°C. This was initially attributed to the CTA, however, later results suggest the CTA is not the cause of the thermal instability. The viscosity of 5 was measured by rheometry.

The viscosity of the semi-solid 5 prepared initially was 1.1 Pa.s at 150°C while the liquid 5 prepared with a modified procedure was 4.8 × 10⁻² Pa.s at this temperature. SEC showed the semi-solid 5 had a broad molecular weight distribution with an *Mn* of 1600 g/mol, while the liquid 5, which also had a similarly broad distribution, had an *Mn* of only 900 g/mol.

Synthesis in VP/1-hexene co-oligomer

Oligomer 5 was employed as a reaction medium for the synthesis of low molecular weight compounds by condensation, aromatic nucleophilic substitution (ArSn), and

Table 7 Polymerizations in VP/1-hexene oligomers^a

Reactant pairs	Medium	Solubility ^b reactant/product	Product viscosity ^c	Product yield (%)	Oligomer recovery (%)
TPE-R/BTDA	6	s/s	0.3	—/100	94
TPE-R/ODPA	NMP	s/s	0.3	—/100	92
	5	s/s	0.3	—/100	92
TPE-R/6FDA	NMP	s/s	0.7	—/—	—/—
	5	s/n	—	—/—	—/—
FDA/BTDA	NMP	s/n	0.4	—/—	—/—
	5	s/n	0.2	—/100	94
FDA/ODPA	NMP	s/n	0.1	—/95	92
	5	s/n	0.2	—/95	92

^aAll polymerizations were done at 180°C for 2 h and at 20% (w/w)^bConsidered soluble (s) if optical transparency was retained at room temperature, and insoluble (n) if opaque at any temperature^cInherent viscosity in NMP (0.5 g/dL) at 30°C

aliphatic nucleophilic substitution (Sn₂). All reactions were done in 5 and in NMP under the same reaction conditions. The results are summarized in Table 6.

Aromatic nucleophilic substitutions were carried out between *p*-chloronitrobenzene (*p*-CNB) and potassium methoxide (K-MeO). After a crude aqueous extraction from the oligomer a 44% product yield was recovered, while a 69% yield of product was recovered from the control by removal of the NMP under reduced pressure.

Aliphatic nucleophilic substitution (Sn₂) was carried out with bromobutane (BrBu) and sodium iodide (NaI), to give only a 29% yield of isolated product.

Several condensation reactions were studied, including both amidation and imidization. Amidation was carried out with benzoic acid (BzA) and butylamine (BuNH₂). Product yields were determined by two methods. A sample of the reaction mixture was evaluated by ¹H n.m.r. and yield prior to product isolation was determined based on the ratio of peaks characteristic of both starting materials and also on peaks associated with the product. The product was then isolated and the final yield of both product and recovered oligomer was determined. The BzA/BuNH₂ reaction was quantitative based on ¹H n.m.r. but was recovered in only 51% yield. Imide reactions were run at 20% (w/w) and 180 ± 10°C for 2 h with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic dianhydride (ODPA), and 4-methoxyaniline (Me-An) as reactants. All reactants and products were soluble, and higher solids concentrations appeared possible. Based on n.m.r. results the yields were quantitative, although, presumably due to the small reaction scale and crude extraction techniques in some instances less than quantitative yields were isolated. The oligomer was recovered for recycling and the recovered yield was generally adequate, considering the crude extraction techniques, but further improvements are anticipated when the oligomer properties and recovery techniques are optimized.

Polyimide polymerizations were carried out in oligomers 5 and 6 (Table 7). The monomers were 1,3-bis(4-aminophenoxy)-benzene (TPE-R), 9,9-bis(4-aminophenyl)fluorene (FDA), 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), BTDA and ODPA. Polar monomers (TPE-R, ODPA and BTDA) and the polymers from them showed complete solubility at 20% (w/w). Less

polar monomers such as 6FDA and FDA were soluble but during the reaction the products phase separated in both oligomeric solvent and in NMP. The oligomer solvent and product polymer were separated by stirring in an ethanol/water mixture and filtering. The product was collected in high yield, but the oligomer recovery, following removal of the ethanol/water under reduced pressure, was less than desired. Control reactions were carried out in NMP and the product isolated by removal of the solvent under reduced pressure. The inherent viscosity of all the polymers prepared were measured after resolating the products in NMP.

The overall results from polyimide syntheses were mixed. Two polyimides retained solubility in the oligomer, and in both instances the measured inherent viscosity was only 0.3 dl/g. The model reactions gave quantitative yields of product so high molecular weight polymer should have been obtained. If oligomer solvent was retained in the product polymer this might have lowered the measured viscosity, however, one control polymerization in NMP also yielded a viscosity of only 0.3 dl/g and the other was still only 0.7 dl/g. Therefore, the control polymerizations appeared to have low molecular weights too. The results were ambiguous. If the low viscosity from the oligomer solvent was not due to oligomer contamination then the low molecular weight may be due to poor technique or to a stoichiometric imbalance resulting from thermal decomposition of the oligomer, since TGA results indicate some decomposition at 180°C. Definite conclusions have not yet been drawn from the polymerization studies.

The overall results from the syntheses were largely positive, but it was clear that optimal results would require a more polar co-monomer to obtain a water-soluble oligomer. This would facilitate oligomer/product separation. Ideally, the oligomer would also be prepared by a living polymerization route to facilitate control of molecular weight without the need for a CTA which can compromise thermal stability. This would also prevent homo-oligomer fractions. Therefore, a pseudo-living cationic route was employed to prepare a VP/EVE co-oligomer.

Synthesis and characterization of VP/EVE co-oligomer

A co-oligomer from VP and EVE was prepared by a pseudo-living cationic method. Several advantages were expected by switching to a pseudo-living oligomer preparation route. These advantages included better control of molecular weight and polydispersity, which would lower the viscosity of the oligomer, and this control could be achieved without the use of a CTA which was expected to yield a more thermally stable oligomer. Pseudo-living polymerization would also allow control over both EVE content and distribution in the co-oligomer. This would give a much more uniform product and eliminate homo-oligomer product. Furthermore, EVE is more polar than 1-hexene and so better water-solubility should result. These expectations were largely realized, including a much lower oligomer viscosity. The viscosity appeared water-like at 80°C and was measured by rheometry and found to be only 4.2×10^{-1} Pa.s at 80°C, versus a viscosity of 1.1 Pa.s for the semi-solid **5** and 14.8×10^{-2} Pa.s for the liquid **5** at 150°C. The VP/EVE oligomer (**1b**) had a nominal molecular weight of 700 g/mol and an EVE content of ~43 mol%, but this value may have a higher than normal error range. The ¹H n.m.r. was complicated with extensive overlap of bands which did not permit a reliable analysis of the EVE content to be made. However, the EVE homo-oligomer made

Table 8 Model reactions in VP/EVE co-oligomer **1b**

Reaction type	Reactants	% Yield (¹ H n.m.r.)	% Yield (isolated)	% Yield (control) ^a	Oligomer recovery
ArSn	<i>p</i> -CNB/ K-MeO	—	60	69	— ^b
Sn ₂	BrBu/NaI	—	37	35	100 ^c
	BrBu/ K-MeO	—	59	—	100 ^c
Condensation	BzA/ BuNH ₂	100	52	—	100 ^c
	BzA/CHA	—	52	56	—

^aControl reaction done in NMP

^bCollected by precipitating model compound in water/ethanol and filtering of the insoluble product, followed by distillation of water/ethanol out of the filtrate. The salt by-products were not separated from the oligomer

^cProduct collected by extraction, but the salt by-product was not separated from the oligomer

under similar reaction conditions was water-insoluble, while the co-oligomer was completely water soluble, so it is unlikely that the EVE content could be significantly greater than 43%. However, despite the fact that no CTA was employed, the thermal stability was less than anticipated. The oligomer showed an onset of decomposition at ~150°C. Therefore, this oligomer was not suited for high temperature reactions such as the polyimide synthesis. Nevertheless, it was an excellent solvent in all other ways, completely solvating every solute employed with the 1-hexene co-oligomers and several other solutes as well. The source of the thermal instability is not yet known conclusively, but is under investigation.

Co-oligomer **1b** was employed (*Table 8*) as a reaction solvent in the same aliphatic nucleophilic substitutions, aromatic nucleophilic substitutions, and condensation reactions previously done in **5**, to permit a comparison to be made. The aromatic nucleophilic substitution between *p*-CNB and K-MeO was repeated, and the isolated yield increased from 44% to 60%, which compares well with the 69% yield isolated from NMP. Aliphatic nucleophilic substitutions were done between BrBu with both NaI and K-MeO. The isolated yield with NaI increased from 29% in **5** to 37% in **1b**, which compares well to the 35% yield obtained in NMP. The amide condensation between BzA and BuNH₂ was repeated and gave essentially the same results as obtained in **5**. Here a 52% yield was isolated as compared with a 51% isolated yield in **5**. A second amidation was done between BzA and cyclohexylamine (CHA). Again, a 52% yield was isolated, while a 56% yield was isolated from NMP. The imide condensations were not repeated due to the lower thermal stability of the VP/EVE co-oligomer.

CONCLUSIONS

VP-rich co-oligomers were prepared and employed as synthetic reaction media. The VP-rich oligomers functioned effectively as reaction media in aromatic and aliphatic nucleophilic substitutions, and in condensation reactions. The product yields in oligomeric solvents were the same, within experimental error, as the yields obtained in NMP. In the case of polymerizations in oligomers the results were less satisfactory. The viscosity data on the product polymers showed the polyimides were low molecular weight, despite the fact that model compounds gave quantitative yields. It is possible that the polyimide was contaminated with oligomer which lowered the measured viscosity. However, the

molecular weight may also have been low due to oligomer decomposition disrupting the monomer stoichiometry. Further research is underway to improve both oligomer thermal stability and oligomer/product separation methods.

It was evident from the research carried out so far that solubility of polar monomers is improved when the polarity of the co-oligomers is not diminished by use of CTA and less polar co-monomers. While the non-living oligomer synthesis does not give control over the polydispersity of the oligomer, modifications of the synthesis allowed a low viscosity oligomer to be prepared and, from multiple syntheses of this oligomer (**5**) the properties were reproducible. Living polymerization methods are nevertheless preferred due to the greater degree of control over co-monomer distribution, molecular weight, and polydispersity.

Low molecular weight products are separable from the oligomer media by distillation. If the oligomer is designed to be water-soluble or water-miscible, products which are not separable by distillation can be separated efficiently from the reaction medium by aqueous extraction.

The concept of using oligomeric solvents is general, so any monomer which can be reacted by any means to a low molecular weight oligomer and yield repeat units which are similar to a targeted conventional solvent could function as an oligomer solvent. This first study on oligomeric reaction

media focused on an NMP-like oligomer to demonstrate the feasibility of using oligomers as solvents, and has shown that oligomeric solvents can be used as reaction media in place of liquid solvents. However, efficient, cost-effective, and environmentally benign product-oligomer separation and purification methods must also be developed. Research is underway on MEK-like oligomers to further investigate structure/property relationships, to determine the source of the thermal instability observed here, and also to develop efficient, environmentally benign separation and purification methods to show that the oligomers can be recycled and be cost-effective to use. Author please cite Ref ³ in text.

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