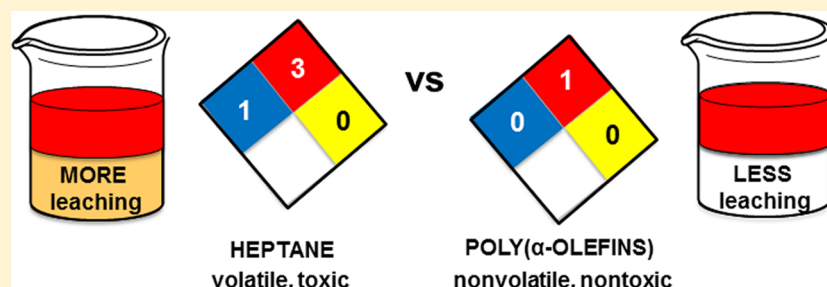


Alternatives for Conventional Alkane Solvents

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S Supporting Information



ABSTRACT: The studies described in this paper show that hydrocarbon oligomers are alternatives for low molecular weight alkane solvents. These oligomeric solvents are nontoxic, nonvolatile, and recyclable alternatives to heptane in thermomorphic solvent mixtures that use a polar solvent such as methanol, aqueous ethanol, or DMF or in biphasic mixtures that use acetonitrile. Regardless of which polar solvent is used, hydrocarbon oligomers like poly(α -olefin)s (PAOs) exhibit very low leaching into the polar phase. UV–visible spectroscopy studies show that these solvents have the solubility properties of heptane. For example, PAOs dissolve heptane soluble dyes and quantitatively separate them from polar phases in thermomorphic solvent mixtures. PAOs either as pure solvents or as additives in heptane act as antileaching agents, decreasing the already low leaching of such dyes into a polar phase in heptane/polar solvent mixtures. These oligomeric hydrocarbon solvents were also compared to heptane in studies of azo dye isomerization. The results show that thermal isomerization of an azo dye occurs at the same rate in heptane and a PAO. Further studies of carboxylic acid promoted dye isomerization in heptane and a PAO show that low molecular weight and oligomeric carboxylic acids are kinetically equivalent at accelerating this isomerization. The results suggest that these and other hydrocarbon oligomers behave as solvents like their low molecular weight nonpolar hydrocarbon solvents and that they can be substituted successfully for conventional solvents like heptane.

INTRODUCTION

Solvents are a ubiquitous part of many if not most chemical processes. They serve useful roles in mitigating exotherms, in providing a suitable milieu for reactions, and in controlling relative concentrations of reacting species. They are essentially required in homogeneous catalysis. However, solvents pose environmental issues and introduce additional costs in any system. Ideally, they should be easily recyclable by a simple physical process. In practice, they often have to be recovered by energy intensive processes like distillation. If they are not recovered, they are disposed of as chemical waste. Lists of greener and more environmentally benign solvents that include new types of solvents as well as more benign and more sustainable organic solvents exist.^{1–3} However, it is difficult if not impossible to design solvents that have all the desired criteria for a green solvent.³ For example, sustainable bioderived organic solvents are often still volatile and as such can introduce unwanted pollutants into the environment.

This paper describes a series of studies of liquid oligomeric hydrocarbons that can serve as substitutes for conventional alkane hydrocarbon solvents. These alternative solvents are greener than typical hydrocarbon solvents such as hexane or

heptane. As solvents, they are as good as or as bad as these conventional alkane solvents. They readily dissolve alkane soluble species and behave as nonsolvents toward polar substrates. Reactions in oligomeric hydrocarbons and in heptane also occur at the same rate. Specifically, thermal or acid-promoted azo dye isomerizations in heptane and in an oligomeric hydrocarbon solvent occur at the same rate. However, oligomeric hydrocarbon solvents have some significant advantages over their low molecular weight alkane analogs. First, they are nonvolatile and relatively nontoxic.^{4,5} Second, unlike lower molecular weight alkanes, they do not significantly contaminate polar phases when used in conjunction with polar solvents. This is true when the nonpolar and polar solvents are separated by a liquid/liquid separation after heating an initial biphasic mixture to form a single phase and then cooling to reform the biphasic mixture (a thermomorphic process).⁶ Finally, when used under thermomorphic conditions with soluble hydrocarbon oligomer-tagged dyes that we have shown are surrogates for phase-anchored

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catalysts,⁷ they lower leaching of the hydrocarbon phase anchored dye into the polar phase—a potential advantage in homogeneous catalysis with hydrocarbon phase anchored catalysts.

The volatility, toxicity, and sustainability issues associated with conventional solvents have spawned the development of a variety of alternative and potentially more environmentally benign solvents or solvent systems in recent years.^{1–3} These include ionic liquids,⁸ supercritical fluids like scCO_2 ,⁹ water (often with surfactants),¹⁰ deep eutectic solvents,¹¹ fluorinated solvents,¹² and polymers.¹³ Each of these alternatives has significant advantages as well as some possible disadvantages. Many of these alternatives have been used in industrial scale processes.

Ionic liquids provide an excellent medium for polar reactions. They can be costly but have the advantages of nonvolatility and separability by simple gravity separations. Their structures are easily varied through synthesis, affording additional versatility and tunability.^{8,14} Supercritical fluids like scCO_2 are industrially used alternative solvents and have been used in applications that range from catalyst to solvent intensive processes like extractions to commercial dry cleaning.^{9,15–17} While scCO_2 requires a pressurized apparatus and depressurization/pressurization cycles in use and recycling, CO_2 has the advantage of being an abundant resource and is both recyclable and sustainable. Water is even more common as a solvent. It can be recycled and is sustainable. While it is not always the most suitable solvent for organic chemistry, the use of surfactants addresses many of these concerns.¹⁰ Its solvent properties are also tunable by the addition of appropriate cosolvents.¹⁸ Large scale transition metal catalyzed reactions using water under biphasic conditions too can be effective as seen in aqueous biphasic catalysis.¹⁹ Less polar milieu have also received attention. For example, fluorinated solvents and fluorinated systems have received significant attention in part because the bulk of these solvents can be recovered in biphasic separations. These simple gravity-based separations for fluorinated solvents and the high solubility of many gases in fluorinated solvents make them attractive candidates for catalytic systems.^{12,20} Lists of solvents that more closely resemble conventional organic solvents but that can be derived from nonpetroleum sources or that are relatively nonhazardous have also been published.² These solvents are in many cases derived from biobased resources. While such solvents often have lower toxicity than a conventional solvent they replace, these solvents still have the volatility issues common to other low molecular weight organic materials. Finally, there is precedent for the use of polymeric solvents. The most common example, poly(ethylene glycol) (PEG),¹³ addresses the volatility issues associated with low molecular weight solvents. PEG has the attractive feature that it resembles common polar solvents. However, separation of polar products from such solvents is not always simple and in many cases involves use of another solvent.

Our recent work has focused on designing soluble polymer-bound catalysts that can be used in a fully miscible solvent mixture yet separated in a biphasic separation step after a homogeneous catalytic reaction.²¹ This work used inexpensive oligomeric phase tags to derived from heptane soluble oligomers or polymers. With such phase tags, it is possible to effect a biphasic recovery of reagents or catalysts that have high alkane phase selective solubility if they have a stable resting state or to separate catalyst and ligand residues from polar phase soluble products.^{22–25}

A disadvantage of these procedures is that they use alkanes like heptane as the nonpolar phase. While much of this solvent can be recovered and reused, it has some undesirable characteristics due to its volatility. Moreover, a portion of it cannot be readily recovered because it partitions into the polar phase and is lost.

Some of our prior work suggested that hydrocarbon oligomers could be a sustainable alternative to a conventional alkane solvent like heptane. One example was our observation that a commercially available low melting point polyethylene wax²⁶ could recover catalysts in a nonvolatile and nontoxic solid paraffin-like matrix that can both protect a catalyst from adventitious decomposition by polar reagents and effect a simple filtration based separation.^{27–32} We subsequently showed that these waxes can be used as cosolvents,^{29–32} reducing metal leaching in processes others described as “commercially viable”.³³ These PE_{Olig} cosolvents also appeared to decrease leaching of homogeneous catalysts.^{29–31}

We more recently reported that the “antileaching” effect seen with polyethylene oligomer cosolvents is also seen when liquid hydrocarbon oligomers are added to a thermomorphic solvent mixture. Those studies showed reduced leaching of either an polyisobutylene (PIB)-bound azo dye or $\text{Ru}(\text{bpy})_3\text{Cl}_2$ complex into a polar phase when a polyolefin oligomer was added to thermomorphic mixtures of heptane and polar cosolvents.³⁴

Prior work on alternatives to alkane solvents has most commonly focused on bioderived solvents that mimic existing alkanes in terms of their molecular weight and volatility. Hydrogenated terpenes are a common example of such alternatives.³⁵ While these solvents are derived from sustainable sources and have useful properties, our preliminary work described above suggested to us that oligomeric hydrocarbons too could be useful greener alternatives to low molecular weight alkane solvents.

Here we describe detailed studies of this possibility, studying polypropylene (PP) oligomers, PIB oligomers, and readily available poly(α -olefin)s (PAOs) as solvents and cosolvents. Our results show that inexpensive polyolefin oligomers can indeed be used like heptane as solvents. These studies show that polyolefin oligomers are as functional as heptane as solvents and that they do not themselves appreciably leach into a polar phase. These studies also show that these oligomeric hydrocarbon solvents themselves or as additives reduce leaching of PIB-bound azo dyes that serve as surrogates of PIB-bound ligands, catalysts, and reagents. Finally, studies of both thermal and acid promoted dye isomerization show that reactions in these oligomeric solvents mirror reactions in heptane.

■ RESULTS AND DISCUSSION

In considering alternatives to simple alkane solvents we had several criteria. First, we wanted materials with low volatility. That criterion can be met simply by using higher minimal vapor pressure. Second, we wanted to use liquid molecular weight hydrocarbon oligomers that have molecular weight hydrocarbon oligomers that have hydrocarbon oligomers because we wanted to effect separations using a simple gravity separation. We have previously shown that polyethylene oligomers (PE_{Olig}) with molecular weights of ca. 500–2000 can function as cosolvents or solvents.^{29–32} However, these materials require separation by filtration, a process that can be problematic when fine particles form.³¹ Third, if an oligomeric hydrocarbon were to be useful, it should have solvent properties like heptane and

dissolve the same things heptane does and does not. Fourth, while an oligomeric hydrocarbon cosolvent is likely to have higher viscosity than heptane, its viscosity should be modest or manageable when used as part of a solvent mixture under the reaction conditions. Fifth, if an oligomeric hydrocarbon alternative solvent were nonvolatile, it could not be removed from a product phase by evaporation as is the case with heptane. Thus, contamination of a polar phase has to be minimal to avoid the need for more purifications of products that might be in that polar phase. Sixth, an alternative hydrocarbon solvent or cosolvent should mimic heptane in terms of creating an appropriate reaction environment. Finally, an alternative to a conventional alkane ideally would be nontoxic, recyclable, inexpensive, biodegradable, and sustainable. As we show below, hydrocarbon oligomers meet many or most of these goals as alternatives to conventional alkane solvents.

The main focus of this work is a particular class of oligomeric hydrocarbons, poly(α -olefin)s (PAOs).³⁶ These materials generally meet the criteria above. They are also inexpensive and commercially available.^{37,38} Conventional alkanes like hexane and heptane have inhalation toxicity.^{39,40} Hexane in particular is not recommended as a solvent due to its volatility and neurotoxicity.³⁹ PAOs in contrast are nonvolatile and do not have inhalation toxicity due to their low vapor pressure. They also have low oral toxicity.^{4,5} Finally, unlike alkanes PAOs are physically recyclable by a gravity separation as discussed below.

PAOs are prepared on a large scale from 1-alkenes most often for use as lubricants. They are inexpensive. Their synthesis is carried out with acid or with transition metal catalyzed oligomerization reactions. Complex mixtures of constitutional isomers form, even in a dimerization.⁴¹ Nonetheless, various PAOs with characteristic viscosities, average molecular weights, boiling points, and modest dispersity are available.

The linear α olefins or 1-alkene precursors of PAOs are most often derived from ethylene via processes like the Aufbau or SHOP processes.^{42,43} The source of ethylene is determined by economics. Currently ethylene is derived from nonrenewable resources in the U.S. However, the economics of ethylene production are such that ethylene derived from bioresources can be competitive in cost.⁴⁴ Thus, while ethylene derived 1-alkenes are not now biobased, ethylene derived 1-alkenes could be derived from sustainable resources if biobased ethylene became competitive with fossil resource derived ethylene. Alternative biobased routes to 1-alkene precursors also exist. For example, a metathesis route to 1-alkenes has been described by Elevance,⁴⁵ who are already advertising their bioderived 1-alkenes. Other catalytic processes leading to 1-alkenes from bioresources have also been described.⁴⁶ Finally, naturally occurring C₈–C₂₀ alcohols could form the alkene precursors of these hydrocarbon oligomers.

PAOs have advantages over alkanes as described above that make them greener and potentially sustainable solvents. However, like all alternative solvents, they have some potential disadvantages too. Specifically, their lack of bioavailability, especially for the larger PAOs described below, limits their biodegradability.^{38,47} While lower molecular weight PAOs are biodegradable, the higher molecular weight PAOs degrade more slowly and could accumulate in the environment though they reportedly do not bioaccumulate in aquatic organisms.³⁸ Second they are more viscous than conventional alkanes like

hexane or heptane and most conventional solvents. The viscosity of what we suggest is a preferred PAO solvent in the studies below is 10 cSt at 100 °C, a viscosity like that of olive oil at 95 °C (9.5 cSt).⁴⁸ Third, they are flammable. However, the flash point of PAOs is >150 °C while heptane has a flash point of –4 °C.³⁷ Finally, PAOs without the addition of another cosolvent are simply alkanes. Thus, PAOs will not be any better than hexane or heptane as pure solvents for even modestly polar organic molecules.

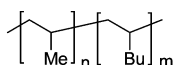
Our studies focused on three PAOs (cf. Table 1) with intermediate molecular weight on a longer list of PAOs that are

Table 1. Poly(α -olefin) (PAO) Alternative Solvents

molecular weight (M_n)	dispersity index	viscosity at 100 °C (cSt)	density (g/mL)
687 (1)	1.12	10	0.84
1758 (2)	1.35	40	0.85
2505 (3)	1.47	65	0.85

available from Exxon Mobil.³⁷ Similar PAOs are available from other sources.³⁸ These inexpensive commercially available compounds come in a variety of molecular weights varying from M_n values of 280 to 4100 Da with dispersity values that range from 1.12 to 1.82 \bar{D} . These materials have a range of viscosities that vary from 2 to 156 cSt at 100 °C. These viscosities will increase on cooling, but here, we use the reported 100 °C viscosity values, as they are most relevant to processes that might involve heated thermomorphic solvent mixtures. The viscosity of olive oil is comparable to that of PAO 1 at ca. 100 °C. Depending on the specific PAO and whether the PAO is used with or without a cosolvent, viscosities of some PAOs as pure solvents or most PAO–cosolvent mixtures are manageable. Three of these PAOs 1–3 were used in the following studies. PAO 3 which has a molecular weight of 2505 Da has too high a viscosity to make it a useful solvent for ambient temperature reactions. However, it could be useful as a cosolvent. PAO 1 with a molecular weight of 687 Da has a viscosity similar to that of olive oil. PAO 2 of molecular weight 1758 Da has an intermediate viscosity. All of these PAOs were colorless liquids. They are all fully hydrogenated, and in ¹H NMR spectroscopy, their signals all occur between 0.8 and 1.4 δ .

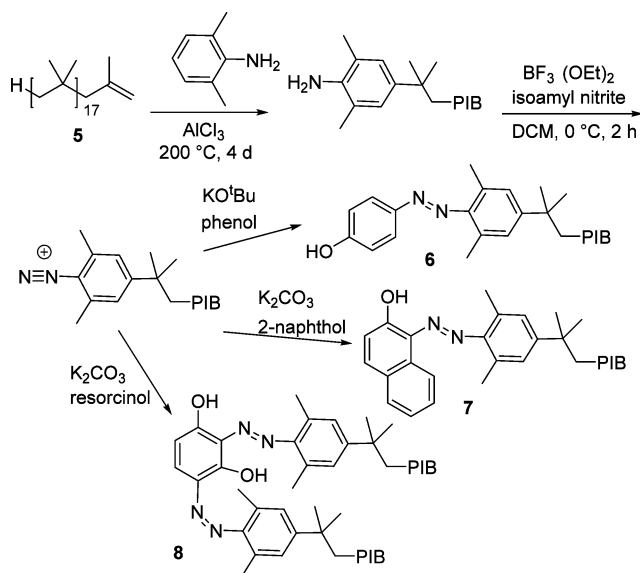
Our studies also included two other polyolefin oligomers as solvents or cosolvents that do not meet all our criteria but that have been used in prior work. One example is a propylene–hexene random copolymer 4 that is like a catalyst support others have used. This polymer contains alkene end groups derived from either propylene or hexene units.⁴⁹ We obtained 4 as a 800 Da material from Baker-Hughes. It has a 25 °C viscosity that is qualitatively similar to that of 1. Oligomer 4 has the disadvantage of containing a terminal alkene group, and it is not commercially available, so its use in our studies was limited. Polyisobutylene (PIB) 5 both with a terminal double bond and in a hydrogenated form is available too. While we have used polyisobutylene (PIB) as a ligand and while PIB derivatives are commercially available, nonvolatile, and nontoxic,⁵⁰ vinyl-terminated PIB with molecular weights of 1000 and 2300 Da have viscosities of 190 and 1500 cSt at 100 °C, viscosities that are too high for PIB to be used as a pure solvent and, in the case of PIB₂₃₀₀, too high to be used as a significant component even in solvent mixtures.



4 (a random copolymer with a 16:1 ratio of propylene and 1-hexene)
(end groups are not shown)

PAOs 1–3, the PP oligomer **4**, and PIB₁₀₀₀ (**5**) were first examined as solvents for PIB-bound azo dyes that were synthesized from PIB oligomers containing a terminal 2,6-dimethylaniline group (Scheme 1).⁵¹ These initial studies used dyes 6–8. All three PAOs 1–3, the PP oligomer **4**, and PIB **5** readily dissolved these dyes.

Scheme 1. Synthesis of Polyisobutylene (PIB)-Bound Azo Dyes 6–8



Next we examined the use of these PAOs 1–3, the PP oligomer **4**, and PIB₁₀₀₀ **5** with other cosolvents (Table 2). The

Table 2. Solubility of Oligomeric Hydrocarbon Alternative Solvents with Conventional Solvents

solvent	oligomer	solubility
heptane	1, 2, 3, 4, or 5	Y ^a
toluene	1, 2, 3, 4, or 5	Y ^a
dichloromethane	1, 2, 3, 4, or 5	Y ^a
tetrahydrofuran	1, 2, 3, 4, or 5	Y ^a
methanol	1, 2, 3, or 4	thermomorphic ^b
ethanol	1, 2, 3, or 4	thermomorphic ^b
isopropanol	1, 2, 3, or 4	thermomorphic ^b
DMF	1, 2, 3, or 4	thermomorphic ^b
acetonitrile	1, 2, 3, 4, or 5	N
water	1, 2, 3, 4, or 5	N

^a1 g of the PAO visually dissolved in 1 g of the low molecular weight solvent at room temperature. ^b1 g of the PAO mixed with 1 g of the low molecular weight solvent formed a homogeneous solution on heating to ca. 100 °C.

PAOs, the PP, and PIB₁₀₀₀ **5** were fully soluble in alkanes, toluene, dichloromethane, THF, and toluene when a 1/1 (w/w) mixture of the PAO and solvent was prepared. A 1/1 (w/w) mixture of the PAO and methanol, ethanol, isopropanol, DMF, acetonitrile, and water formed biphasic mixtures at room temperature. Oligomers 1–4 all showed varying levels of

thermomorphic behavior with alcohols with temperature dependent solubility behavior that was similar to that of heptane. However, an initial concern was that hydrocarbon oligomers, like heptane, could contaminate a polar phase.

This is a concern because if there were significant contamination, such hydrocarbon oligomer contaminants would have to be removed from products by extractions with alkanes or by chromatography. Such additional purification steps would be a significant liability for an alkane solvent substitute. To test this issue, we used a version of a ¹H NMR experiment that relies on the 1.1% natural abundance of ¹³C. We have previously used this technique to assay end functionalized PEG *M_n* values, and others have used it to analyze trace impurities in products in asymmetric synthesis.⁵² In this experiment, we examined a 10 mL solution of a 3:2:5 (by weight) thermomorphic mixture of cyclooctane, **4**, and DMF. When this mixture was heated to ca. 70 °C, a monophasic solution formed. On cooling to room temperature, it again became biphasic. At that point, it was possible to isolate the DMF phase and show by integrating the peaks at 8.0 δ versus the cyclooctane peak at 1.3 δ the amount of the cyclooctane that had partitioned into the denser DMF phase. In addition to the cyclooctane singlet at 1.3 δ, two satellite peaks due to the 1.1% ¹³C in cyclooctane appeared. When the ¹H NMR spectrum in the 0.5–2.0 δ region was carefully examined, the cyclooctane peak and the ¹³C satellite peaks were the only signals seen. No peaks attributable to the leaching of <0.1% of **4** and to the presence of less than 100 ppm of **4** in the DMF phase. This level of contamination of **4** in the polar phase was judged to be insignificant.

This promising result of little contamination of the polar phase by **4** led us to quantitatively study the extent to which PAO solvents 1–3 significantly contaminate a polar phase (cf. Table 3). To carry out these studies, we used a version of this ¹H NMR experiment. In this case we relied on the 1.1% natural abundance of ¹³C in MeOH, DMF, and CH₃CN and examined 6 g of a 1:1 (w:w) mixture of the PAO and MeOH, DMF, or CH₃CN as the polar solvent. When the PAO and MeOH or DMF were heated, these solvent mixtures exhibited thermomorphic character and a monophasic solution formed at 100 °C. On cooling to room temperature, these solutions became biphasic. The PAO/CH₃CN mixtures were always biphasic. They were heated with stirring for 24 h at ca. 100 °C. We believe this heating and stirring time was sufficient to reach phase equilibrium for the PAO and CH₃CN mixture, since experiments carried out for 48 h showed no significant change in the % leaching of PAO 1, 2, or 3 into CH₃CN. After cooling the solvent mixtures to ambient temperature, the polar phase was isolated and the amount of the PAO present was determined by integrating the satellite of one of the polar solvent peaks and comparing it to the integration of the known PAO peak. We did not determine if cooling to room temperature lowered this level of contamination of PAO in CH₃CN. However, since we believe that the solubility of PAO in CH₃CN does not increase on cooling, the trace amounts of PAO in CH₃CN we measure are a maximum amount of contamination for this polar phase. Table 3 shows the mass of PAOs that leached into the various polar solvents as well as the percent leaching of the PAOs in each polar phase. These analyses correspond to the presence of 50–200 ppm PAO 1 in any of these solvents. This ppm value would decrease if the PAO were used as a cosolvent. We speculate that the percent

Table 3. ^1H NMR Analysis of PAO Leaching into the Polar Phase of a Polar Solvent/PAO System

oligomer	polar solvent ^a	PAO in the polar phase (mg) ^b	PAO leaching (%) ^{c,d}
1	MeOH	1.0	0.03
2	MeOH	0.4	0.01
3	MeOH	0.5	0.02
1	DMF	0.3	0.01 ^d
2	DMF	2.0	0.06
2 ^e	DMF	3.4	0.12
3	DMF	24.0	0.80
1	MeCN	1.0	0.03 ^d
2	MeCN	0.4	0.01 ^d
3	MeCN	0.4	0.01 ^d

^aA biphasic mixture of 3 g of the PAO and 3 g of the polar solvent was heated to form a single phase and then cooled to reform a biphasic mixture. Then a drop of the polar solvent solution was removed for ^1H NMR spectroscopic analysis using CDCl_3 as the solvent. These analyses were carried out at ambient temperature with the exception of the methanol samples which required analysis at $-30\text{ }^\circ\text{C}$ to shift the methanol $-\text{OH}$ peak away from the PAO peak being analyzed. ^bThe mg amount of the PAO in the polar phase was calculated by setting the integral for the formyl H of DMF or the methyl singlets of MeOH or CH_3CN to 100 and comparing 1.08% of this integral to the integration of any detectable PAO peak between 0.8 and 1.4 δ . The Supporting Information also includes an estimate of the percent PAO leaching based on a second calculation that used the measured integrals of the ^{13}C satellites of the formyl H of DMF or the methyl singlets of MeOH or CH_3CN to the integration of any detectable PAO peak between 0.8 and 1.4 δ (Table S1). The PAO leaching values measured this way were very similar or identical to the results using a base peak with an integration of 100. ^cThe percent leaching of the PAO was based on the mg amount of PAO in the polar phase relative to the 3 g of PAO in experiments that used equal weights of the PAO and polar solvent. ^dAnalyses of the PAO leaching where the PAO leaching is less than 0.03% have to be considered as estimates because of the difficulties in integrating the small PAO signal. ^eEstimates of leaching for this sample of PAO used PAO that was purified by extraction with acetonitrile for 3 d in a liquid/liquid extraction apparatus.

leaching and the ppm of PAO in these experiments would also be further decreased by the addition of some water or salt to the polar phase. In any case, only a small amount of PAO leached regardless of which polar solvent was used, showing that PAOs as alternative solvents do not significantly contaminate a polar phase in a thermomorphic or biphasic solvent mixture.

Our prior studies of polyethylene oligomers and of liquid polyolefin cosolvents suggested oligomeric cosolvents could have an additional feature not seen with heptane alone. Specifically, the several cases where we used polyethylene oligomers as cosolvents as well as experiments with azo dyes and Ru complexes suggested that oligomers added as cosolvents could reduce hydrocarbon polymer-bound catalyst leaching into a polar phase. This antileaching effect was further explored here using the azo dyes 6–8.

To study this antileaching effect, we first examined the leaching of dyes 6–8 from heptane into 10% aqueous EtOH in a thermomorphic mixture. Addition of 3 g of 10% aqueous EtOH to a solution of 20 mg of the azo dye in 3 g of heptane produced a biphasic solvent mixture. Heating this produced a visually monophasic solution. On cooling, this thermomorphic solvent mixture reformed a biphasic heptane/aqueous EtOH solvent mixture. At this point, we analyzed the polar phase

using UV–visible spectroscopy to determine the amount of the leaching of the dye into the polar phase. These studies showed that the azo dye 6 had 7.8% leaching, the azo dye 7 had 1.3% leaching, and the azo dye 8 with two PIB groups had the least leaching (0.2%).

We chose the azo dye 7 having an intermediate amount of leaching in the next set of experiments to study the effect of changing the identity of the polar solvent. We repeated the above experiments this time using the same dye 7, varying the polar solvent identity. Using DMF, MeOH, 10% aqueous EtOH, and CH_3CN as the polar solvent led to 4.7%, 4.1%, 1.3%, and 0.9% leaching, respectively. While the experiment with CH_3CN as the polar phase never involved formation of a homogeneous solution, the 0.9% leaching observed was the limiting value for leaching of 7 after stirring a biphasic mixture of 7, heptane, and CH_3CN for 24 h at ambient temperature.

The experiments above suggested that the use of 7 with a heptane/MeOH thermomorphic mixture would be the most useful solvent mixture to probe the “antileaching” effects of hydrocarbon oligomers. As shown in Table 4, PIB or PIB

Table 4. Leaching of a Polymer-supported Dye into the Methanol Phase in a Methanol/Heptane Polymer Cosolvent Thermomorphic System^a

entry	oligomer cosolvent	% leaching ^b
1	none (heptane only)	4.1
2	PIB-(alkene terminated) (5)	2.3
3	PIB-(CH_2Br terminated)	2.5
4	PIB-(2,6-dimethylaniline terminated)	2.5
5	PIB-(CH_2OH terminated)	2.7
6	PIB-(cresol terminated)	2.8
7	4	2.3 ^c
8	PAO 1	1.9 ^d
9	PAO 2	2.6 ^d
10	PAO 3	3.2 ^d

^a20 mg of the dye and 1 g of the polymer cosolvent were added to 3 g of heptane and 3 g of MeOH. Absorbance measurements were taken after thermomorphic heating at $85\text{ }^\circ\text{C}$ followed by cooling to room temperature and allowing the samples to sit overnight to separate cleanly. All PIB functionalized materials were prepared from PIB alkene of molecular weight 1000 Da, and their syntheses use literature procedures or are described in the Supporting Information. ^bThe percent leaching was calculated by using the known concentration of the dye in heptane and the extinction coefficient of a low molecular weight analog of the naphthol dye in MeOH and has an estimated error of $\pm 0.2\%$. ^cA similar experiment used 1 g of 4, 2 g of heptane, and 3 g of MeOH with a PIB_{2300} -bound naphthol azo dye and had 0.5% dye leaching (ref 34). ^dThis experiment used 20 mg of dye, 1 g of the PAO, 2 g of heptane, and 3 g of MeOH. Absorbance measurements of the MeOH phase were taken after the mixture was heated at $100\text{ }^\circ\text{C}$ to form a single phase and then cooled to room temperature to reform a biphasic mixture. The MeOH phase was isolated at that point, centrifuged to remove any physical PAO contaminant, and analyzed.

additives measurably decrease leaching of dye 7. However, the identity of the terminal functionality on the PIB has a very small effect on the antileaching property of these cosolvents. These same studies show that PAOs 1–3 are similar to PIB or PIB derivatives as antileaching agents. We next set out to more systematically analyze the antileaching effectiveness of PAOs as solvents or cosolvents with heptane. Methanol was again chosen as the polar solvent, and the PIB-bound azo dye 7 was used to monitor the leaching in different systems. Similar to the

previous leaching experiment, 20 mg of the azo dye **7** were added to the nonpolar phase which had varying amounts of heptane and PAO (3 g total). Next, 3 g of methanol were added and the system was heated to 100 °C to form a monophasic solution. Cooling reformed a biphasic mixture where the dye was visually in the PAO phase. After separation of the phases, the methanol absorbance was analyzed by UV–visible spectroscopy to determine the amount of leaching of the azo dye. By varying the amount of the PAO in comparison to heptane, the viability of the PAO as an antileaching agent was analyzed.

The results of the experiments presented in Table 5 showed that as the amount of PAO cosolvent increased in the nonpolar

Table 5. Leaching of the PIB-Bound Dye **7 into the Methanol Phase of a Heptane/PAO/Methanol Thermomorphic Solvent Mixture^a**

PAO	PAO M_n (Da)	heptane/PAO Ratio (g/g)	% leaching of 7 into MeOH ^b
none	–	3.0/0	4.1
3	2505	2.0/1.0	3.2
3	2505	1.5/1.5	2.5
3	2505	1.0/2.0	2.0
3	2505	0.5/2.5	1.5
3	2505	0/3.0	1.1
2	1758	2.0/1.0	2.6
2	1758	1.5/1.5	1.7
2	1758	1.0/2.0	1.5
2	1758	0.5/2.5	1.1
2	1758	0/3.0	0.9
1	687	2.0/1.0	1.9
1	687	1.5/1.5	1.4
1	687	1.0/2.0	1.0
1	687	0.5/2.5	0.8
1	687	0/3.0	0.6

^aThe dye **7** (20 mg) was added to a heptane/PAO or a PAO only phase (3 g total) followed by the addition of methanol (3 g). This biphasic mixture was then heated to 100 °C. During this heating process, the biphasic mixture became one phase. After stirring for several minutes, the thermomorphic mixture was cooled to room temperature. Centrifugation was used to cleanly separate the phases. The MeOH phase was then analyzed by UV–visible spectroscopy.

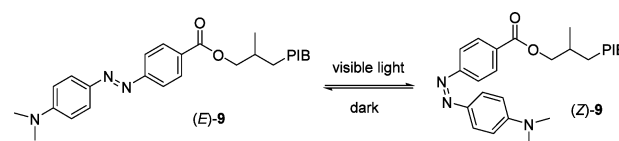
^bThe leaching value reported is the average of three measurements and was calculated based on the original concentration of the dye in heptane using an extinction coefficient for a low molecular weight analog of the naphthol dye in MeOH. This value has an estimated error of $\pm 0.2\%$.

phase, the leaching of the polymer-supported dye into methanol decreased regardless of which molecular weight of oligomer cosolvent was used. PAO **1** was able to reduce leaching of the dye most significantly. When PAOs were used as replacement solvents for heptane the leaching was reduced even more substantially. Again, PAO **1** was shown to be the oligomer solvent with the greatest antileaching ability.

It was also important to understand whether reactions in a PAO phase would occur as they do in heptane, the nonpolar thermomorphic solvent we have most commonly used for catalysis studies and catalyst recycling. To address this question, we used a PIB ester of *p*-methyl red **9** that we had previously used as an additive in surface modification of polyethylene and as a probe of thermomorphic separations with PIB and polar solvents.^{53,54} These studies used PAO **1** and first studied the

thermal isomerization of **9** in heptane and in PAO **1** (Scheme 2).

Scheme 2. Light Induced Isomerization of a PIB-bound *p*-Methyl Red Azo Dye **9**



The results obtained showed that the rate of the isomerization remained constant whether heptane or PAO **1** was used as solvent. The isomerization rate in heptane is $2.2 \times 10^{-4} \text{ s}^{-1}$ while the rate in PAO **1** is $2.3 \times 10^{-4} \text{ s}^{-1}$.

To further probe the possible difference in reaction rates in heptane versus a PAO, we also examined acid-promoted dye isomerizations in which selected acids were added to study the rate of acid-promoted isomerization of azo dye **9** in both heptane and PAO **1**. As shown in Figure 1, regardless of

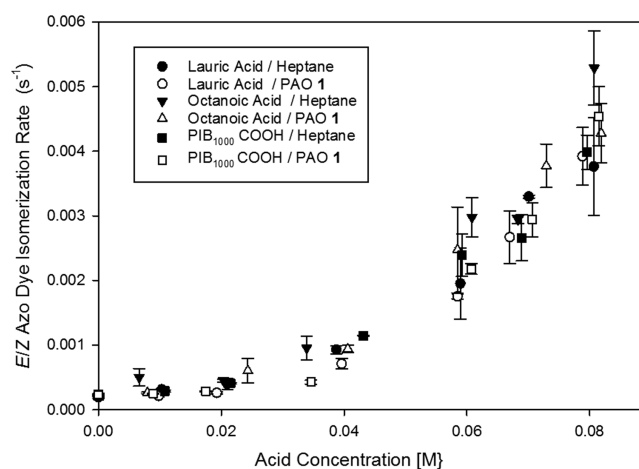


Figure 1. Comparison of carboxylic acid promoted isomerization rates using different nonpolar phase soluble carboxylic acids in either PAO **1.**

whether the carboxylic acid used was octanoic acid, lauric acid, or a PIB-supported carboxylic acid, the rate of isomerization of **9** increased with acid concentration. The results in Figure 1 showed a nonlinear increase in the observed dye isomerization rate with the concentration of the carboxylic acid. The acid-promoted dye isomerization data and the thermal isomerization data show that these simple reactions in PAO and heptane occur at similar rates, further indicating that these hydrocarbon oligomers can serve as a suitable solvent replacement for conventional volatile hydrocarbons.

As noted above, PAOs are prepared from α -olefins using acidic or transition metal catalysts. In the event some catalyst residues from the PAO synthesis were present, they, like the carboxylic acids, could promote the isomerization rate of the basic dye **9**. In the isomerization studies in Figure 1, we saw no evidence of this for studies of thermal isomerization of **9** carried out in PAO **1**. However, thermal isomerizations in the “as received” PAO **2** and PAO **3** were faster than that in heptane. When triethylamine was added to these solutions, the higher isomerization rate was no longer seen and the thermal isomerization of dye **9** in the amine modified PAO **2** or **3**

was the same as that in heptane or as in PAO 1. This suggested acidic impurities were present in PAOs 2 and 3. We thus examined whether we could remove these impurities from PAOs 2 and 3 by continuous liquid/liquid extraction with acetonitrile. In the event, a 3 d liquid/liquid extraction appeared to remove the presumed acid impurity and thermal isomerization rates in the purified PAO 2 and PAO 3 were the same as that in heptane or PAO 1. Since PAO 2 and PAO 3 are less likely to be used as pure solvents for reactions because of their viscosity, we did not further examine these two solvents in isomerization studies. We did however examine how they behaved in recycling and in dye leaching below.

Finally, we examined recycling of these PAO solvents. These recycling experiments included five cycles for each PAO. Following the protocols used before, we used 3 g of MeOH as the polar solvent, 20 mg of the dye 7, and 3 g of the PAO solvent. After thermomorphic heating, the solutions were cooled to ambient temperature and UV–visible spectroscopy was used to analyze the concentration of 7 in the MeOH phase of the biphasic mixture. In the second and subsequent cycles, the original MeOH phase was removed and 3 g of fresh methanol were added to the PAO solvent containing the polymer-supported dye to begin the next cycle. The process was repeated until five cycles were complete. The results presented in Figure 2 show that all of the PAOs can be reused.

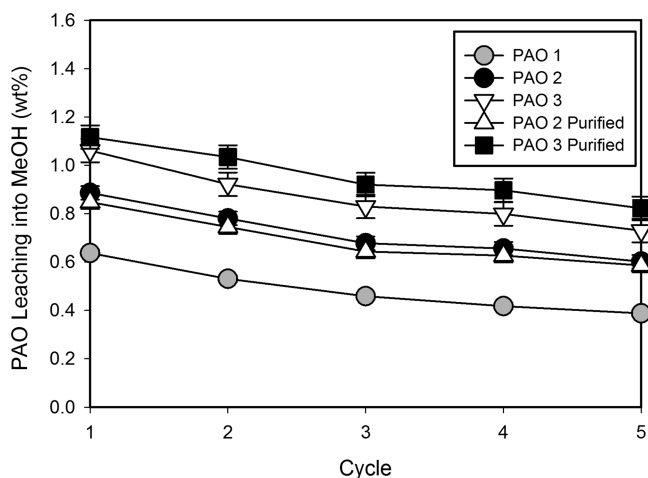


Figure 2. Recycling of PAO oligomer solvents in a PAO/methanol thermomorphic solvent system.

Dye leaching slightly decreased during these five cycles. We believe this behavior is similar to leaching behavior seen with catalysts where the first few cycles have more leaching. We believe this occurs because the PIB-bound species, here a PIB-bound dye, has some dispersity where the lower molecular weight fraction has a small but measurably greater leaching rate. No measurable volume decrease of the PAO phase was seen through these five cycles, a result that is consistent with the trace leaching of PAOs into the polar phase. In similar experiments with heptane, the heptane volume would decrease significantly through this same number of cycles unless heptane-saturated MeOH was used as the polar phase. Purification of PAO 2 and PAO 3 by extraction with acetonitrile for 3 d in a liquid/liquid extraction apparatus had little effect in these experiments.

The changes in dye leaching using purified or “as received” PAO 2 and 3 were either very small or were within experimental error (Figure 2).

CONCLUSION

In summary, the work presented in this paper shows that hydrocarbon oligomers can be used as alternatives for heptane in thermomorphic solvent systems. Detailed studies of one class of such solvents—PAOs—show that PAO solvents behave like heptane in terms of their solubility in other solvents and in terms of what they do or do not dissolve. These studies also show that PAOs do not significantly leach into polar phases. In addition, when used with polymer-bound dyes, PAOs act as antileaching agents reducing the amount of the polymer-bound dye that leaches into a polar phase. These recyclable oligomeric hydrocarbon solvents were also compared to heptane in studies of azo dye isomerization. The results show that thermal isomerization or carboxylic acid promoted isomerization of an azo dye occurs at the same rate in heptane and a PAO. These results indicate that PAOs and other polyolefin oligomers can be a more sustainable solvent choice in comparison with heptane and that they can serve even better than heptane for separation of soluble polymer-bound catalysts in liquid/liquid separations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07967.

Experimental procedures for the synthesis of azo dyes and functionalized polymer cosolvents, general procedures for the setup of UV–visible spectroscopy, and details of the ^1H NMR spectroscopic studies of leaching are provided (PDF)

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Notes

The authors declare no competing financial interest.

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