Novel Catalysts for the Ring-Opening Metathesis Polymerization of Norbornene-Type Monomers

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SYNOPSIS

A novel family of metallate compounds has been developed for use in catalyst systems for the ring-opening polymerization of dicyclopentadiene (DCPD) and other norbornene-type monomers. Examples of these novel catalyst compounds are the organoammonium isopoly- and heteropolymetallates. Applications of these metallates in combination with alkylaluminum-type reducing cocatalysts are found in the production of both solution polymers, and cross-linked resins from reaction injection molding (RIM). These catalyst systems have significant advantages over prior art catalysts. They are highly soluble in DCPD and other norbornene-type monomers, thus eliminating the need for a reaction solvent. They also are insensitive to air and moisture, have unlimited shelf-life in solution in norbornene-type monomers, and do not function as Lewis acids. The chemistry of these catalyst systems is discussed, along with the benefits they provide to the properties of the final polymer products. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Ring-Opening Metathesis Polymerization (ROMP)

The history of ring-opening polymerization can be traced back to the late 1950s and early 1960s in the laboratories of DuPont with the publication of patents to Anderson and Merckling[1] describing the ring-opening of norbornene using a $TiCl_4$/aluminum alkyl catalyst system, and Eleuterio's[2] description of the ring opening of cyclopentene, as well as norbornene.

The investigations of Calderon et al.[3] in the late 1960s led to the discovery of the classic olefin metathesis and ring-opening polymerization catalyst, WCl_6/EtOH/EtAlCl$_2$. This system was first shown to be a highly active catalyst for the ring-opening polymerization of cyclooctene and 1,5-cyclooctadiene, etc.[3] and a variety of other cyclic olefin monomers such as cyclopentene and DCPD.[4a] In related patents, the use of alcohols and phenols is described as a "third component" instead of ethanol.[4b] The use of this type of third component was found to substantially improve catalyst efficiency. Van der Ven and Kohler[5] described the use of hindered phenol modified tungsten halides (e.g., bis(2-isopropylphenoxy)tungsten tetrachloride) in combination with alkylaluminum halide cocatalysts to polymerize cyclopentene.

Minchak[6] described the homo- and copolymerization of cyclopentene, norbornene, and dicyclopentadiene in a series of patents filed in the 1970s. The catalyst used was typically $MoCl_5$ or WCl_6 in combination with an alkylaluminum halide cocatalyst. Preferably the cocatalyst comprised a mixture of diethylaluminum chloride and iodide. Alternatively, elemental iodine was introduced as such into the system. The molecular weight of the polymer was controlled by running the polymerization in the presence of an acyclic olefin such as 1-butene or 1-hexene. Third components (usually referred to as "activators") such as water, alcohols, or phenols were described. Furthermore it was preferred to use Lewis bases such as ethyl acetate, since they cause a brief induction period (typically 1–5 min) that results in better process control and a more uniform product.

More recently the development of one-component, well-defined, isolable alkylidene complexes,

primarily by groups at California Institute of Technology,[7] Massachusetts Institute of Technology,[8] and the University of Strasbourg[9] has ushered in the era of living polymerizations of norbornene-type monomers. Catalysts of this type provide a degree of selectivity,[10] and molecular weight control unattainable with catalyst systems of the Ziegler-type as previously described.

Application of ROMP to DCPD Reaction Injection Molding (RIM)

Probably the first polymerization studies of DCPD were published by Dall'Asta and coworkers.[11] Depending on the choice of catalyst and process conditions, both addition and ring-opening polymerization of DCPD were reported. A partially cross-linked and insoluble ring-opened polymer was formed from a WCl_6 and diethylaluminum chloride catalyst in toluene. In contrast, titanium-based catalysts gave largely addition polymers as did WCl_6 itself (in the absence of a cocatalyst).

Application of ROMP of DCPD to RIM has been outlined by Macosko.[12] RIM polymerization of DCPD uses a two component catalyst system. A soluble procatalyst and cocatalyst, are dissolved in monomer and stored in two separate containers. The two solutions are mixed together and pumped into a mold. The active catalyst forms *in situ,* and rapid polymerization occurs forming a solid part. One advantage of the RIM process over conventional thermoplastic injection molding (TIM) is the low viscosity of the starting materials under ambient conditions that enables the reactants to easily flow into the mold. In contrast, TIM requires considerable energy (heat and pressure) to inject the compounded resins into the mold.

The selection of a suitable catalyst for a RIM process is severely restricted. The need for rapid mixing and homogenization of the reacting mixture, combined with the requirement for very fast reaction rates, prevents using heterogeneous catalysts of the types traditionally used in olefin metathesis of acyclic olefins. The one-component metal-alkylidene catalysts that have resulted in technological breakthroughs in solution polymerization of norbornene-type monomers are also unsuitable for RIM applications since polymerization is initiated as soon as the catalyst is dissolved in the monomer. One exception seems to be the titanocene-based catalyst developed by Grubbs and coworkers that polymerizes only at elevated temperatures.[7a] Hence the catalyst systems of choice are found in the Ziegler two-component catalyst family; typically, the first

component, a halide of a group 6 transition metal (preferably tungsten or molybdenum) is dissolved in one monomer stream, while the second component, typically an alkylaluminum compound (alkyltin hydrides also are commonly used) is dissolved in a second monomer stream.

A number of companies have filed patents claiming the above-described group 6 metal halide catalysts for bulk (RIM-type) polymerization of DCPD, etc. For example, Hercules,[13] Elf Aquitaine,[14] and Teijin[15] have all filed patents describing the bulk (RIM-type) ring-opening polymerization of DCPD and the like using phenoxytungsten chloride catalysts in combination with alkylaluminum halide cocatalysts as well as other components. Shell describes the use of phenol modified tungsten halides in combination with alkyltin hydride cocatalysts.[16]

Despite the activity in the patent literature concerning the application of WCl_6- and $MoCl_5$-based catalyst systems in DCPD RIM, there are problems associated with the use of these catalysts. First of all, these tungsten and molybdenum halides are virtually insoluble in DCPD and similar RIM monomers. This necessitates solubilizing the catalyst, typically by reacting the halides with alkylphenols or adding controlled amounts of suitable complexing solvents, such as ethyl acetate. Further, the Lewis acidity of the group 6 halide-based compounds causes norbornene-type monomers to polymerize prematurely (presumably via a cationic mechanism). Indeed, an early publication by Oshika and Tabuchi[17] reported that norbornene and DCPD were readily polymerized to high molecular weight polymers using simple Lewis acids, such as WCl_6, $MoCl_5$, $ReCl_5$, and $AlCl_3$ without the use of a cocatalyst. A patent assigned to Shell[18] describes the use of group 6 metal oxyhalides such as $MoOCl_3$ and $WOCl_4$, again in the absence of a cocatalyst, to polymerize DCPD and similar monomers. Although the solubility problem can be minimized by complexing the Lewis acidic tungsten halide with a large excess of a suitable Lewis base, the resulting monomer solutions still have limited shelf-lives. We describe herein a novel family of metallate catalysts for the ring-opening metathesis polymerization of norbornene-type monomers that do not suffer from the limitations of the classical group 6 metal halides.

EXPERIMENTAL

General

Silicotungstic acid ($SiO_2 \cdot 12WO_3 \cdot 26H_2O$) was purchased from Fisher Scientific while phosphotungstic

acid ($H_3PO_4 \cdot 12WO_3 \cdot xH_2O$) and sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$) were purchased from Aldrich. The detailed procedures for preparing organoisopolymolybdates, such as $[(C_{13}H_{27})_3NH]_4$ $[Mo_8O_{26}]$, have been published.[19] A general description is given in the Results and Discussion Section. Adogen-340 is a trihydrogenated tallow amine, R_3N, available from Schering Berlin Polymers, where R is a mixture of approximately 5% C_{14}, 30% C_{16}, and 65% C_{18} alkyl chains. For the purpose of this report and the syntheses to be described, Adogen-340 will be represented as R_3N. The approximate combining weight was taken to be 755. All infrared spectra were recorded on a Perkin–Elmer 1800 instrument. Catalyst infrared samples were prepared as a fused capillary film on CsI discs.

Flexural modulus study specimens were tested according to ASTM D790-86. The flexural modulus values were obtained in triplicate, and average values are reported. Izod impact strength was determined on notched specimens at room temperature according to ASTM D256-88. These measurements were made in triplicate, and average values are reported. Dynamic mechanical spectroscopy was performed using a Rheometrics spectrometer in torsion configuration. Temperature sweeps were performed at a frequency of 10 rad/s and a heating rate of 2°C/min with a soak time of 1 min. Modulus curves were determined for each specimen and the T_g (glass transition temperature) was estimated from the maximum of the tan $\delta(G'/G'')$ peak.

$[R_3NH]_3[PW_{12}O_{40}]$

Solid Adogen-340 (15.7 g, 20.8 mmol) was dissolved in approximately 250 mL of warmed toluene (40–50°C) in a 500 mL three-necked round bottom flask equipped with a stirbar and a condenser. A water solution (ca. 50 mL) of phosphotungstic acid (20.0 g, 6.94 mmol) was added to this colorless solution to give a two-phase mixture. The toluene layer became yellow immediately. The mixture was heated to reflux for 30 min. The resulting greenish-yellow toluene layer was separated from the essentially colorless aqueous layer after cooling to room temperature. The aqueous layer was washed with fresh toluene (2 × 50 mL). The toluene fractions were combined and dried over molecular sieves overnight. The toluene layer was decanted from the molecular sieves and rotary evaporated to yield a pale green viscous liquid. Further drying at 60°C under vacuum gave a pale blue waxy solid (24.7 g, 69% yield). IR (cm^{-1}): 2925 vs, 2855 vs, 1468 s, 1080 s, 984 vs, 897 vs, 819 vs br, 722 m, 598 w, 522 m, 511 m, 390 s, 376 m sh, 339 m, 280 w, 268 m.

$[R_3NH]_4[SiW_{12}O_{40}]$

Solid Adogen-340 (13.7 g, 18.1 mmol) was dissolved in a minimum of warm toluene (40–50°C, ca. 200 mL) in a three-neck 500 mL round bottom flask equipped with a stirbar and condenser. A water solution (ca. 50 mL) of silicotungstic acid (20.0 g, 6.04 mmol) was added to the toluene solution to yield two layers. The toluene layer became a pale yellow. The two-phase system was refluxed for 20 min. After cooling, the toluene layer was separated from the aqueous layer. The aqueous layer was washed with additional toluene (2 × 50 mL). The organic layers were combined and dried over molecular sieves overnight. Separation of the pale yellow solution from the sieves, and subsequent rotary evaporation of the toluene left an almost colorless solid residue. Further drying at 60°C under vacuum gave a waxy solid (24.27 g, 68% yield). IR (cm^{-1}): 2920 vs, 2850 vs, 1469 s, 1013 m, 976 s 929 vs, 888 s sh, 798 vs, 723 m sh, 555 w sh, 535 m, 512 w sh, 403 m sh, 388 s, 341 m, 290 w, 248 w.

$H_5[BW_{12}O_{40}] \cdot 26.5H_2O$

The reactant for preparing the organoheteropolyborotungstates, borotungstic acid ($H_5[BW_{12}O_{40}] \cdot xH_2O$) was synthesized using a slight variation of the published procedure. The water content of the yellow solid is thought to be approximately 26.5 moles per mole of borotungstic acid.[20] Solid $Na_2WO_4 \cdot 2H_2O$ (100.0 g, 303.2 mmol) was placed in a 500 mL three-neck round bottom flask equipped with a stirbar and a condenser. Approximately 400 mL of water and 150 g of H_3BO_3 were added. The resulting slurry was heated to reflux to form a colorless solution. The solution was refluxed until no precipitate formed when small aliquots of the solution were treated with dilute HCl (ca. 3 h). The clear solution was cooled to room temperature in 2 h. No significant amount of a solid formed. The solution was cooled to about 5°C for 60 h. A colorless solution was then separated from a colorless solid. After adding 70 g of H_3BO_3 to the filtrate its volume was reduced in half by heating the solution in an open beaker. A large amount of colorless solid was filtered off and washed with 30 mL of ca. 33% H_2SO_4. Addition of the acid to the filtrate resulted in formation of a precipitate that was filtered off. The filtrate was condensed in a rotary evaporator to 50–100 mL at which time a solid formed. The slurry was placed in a separatory funnel and diethylether was added. Addition of ice-cold 37% HCl to the two-phase system yielded a heavy oil that fell to the bot-

tom of the separatory funnel giving three layers. Cold 37% HCl was added until no more oil formed (ca. 30 mL of oil was collected). The oil was separated from the other two layers. An equal volume of H_2O was added to the oil. The diethylether in this solution was allowed to evaporate overnight. The resulting solution was placed under aspirator vacuum in a desiccator with P_2O_5. After several days and repeated additions of fresh desiccant, a yellow solid precipitated that eventually dried to a hard yellow solid as the excess water and HCl were removed (35.2 g, 42% yield). The product was used without characterization in the synthesis of $[R_3NH]_5[BW_{12}O_{40}]$ as described below.

$[R_3NH]_5[BW_{12}O_{40}]$

Adogen-340 (40.2 g, 53.2 mmol) was dissolved in 300 mL of warm toluene (40–50°C) in a 2 L three-neck round bottom flask equipped with a stirbar and

condenser. To this solution was added a slurry of $H_5[BW_{12}O_{40}] \cdot 26.5H_2O$ (35.2 g, 10.5 mmol) in 500 mL of water. The mixture was heated to reflux for 2 h. After cooling, the toluene layer was separated from the aqueous layer. The toluene washings of the aqueous layer were combined with the toluene layer and dried overnight over molecular sieves. Rotary evaporation of the toluene yielded a solid residue that was dried further under vacuum at 60°C to yield a hard, waxy, pale greenish-yellow solid (63.0 g, 90% yield). IR (cm^{-1}): 2923 vs, 2855 vs, 1469 s, 998 m, 955 s, 909 s, 818 vs br, 722 m, 543 m, 509 m sh, 426 w, 390 s, 344 m, 296 w, 248 w.

Polymerization Studies

The general polymerization scheme is illustrated using $[(C_{13}H_{27})_3NH]_4[Mo_8O_{26}]$, a representative organoammonium molybdate catalyst, in combination with a diethylaluminum chloride cocatalyst.
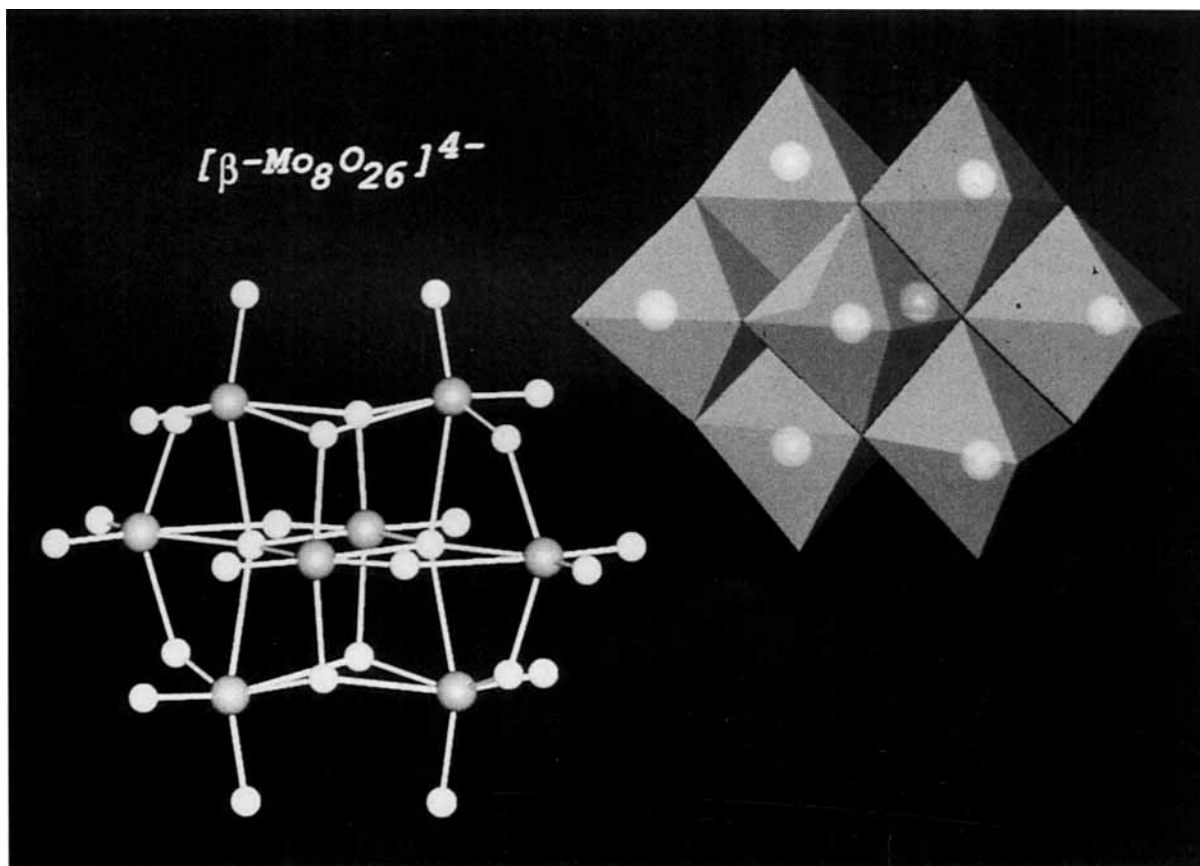
Figure 1 Structure and polyhedral representation of β-$[Mo_8O_{26}]^{4-}$ (crystallographic data from reference 22). The large dark spheres represent molybdenum and the small white spheres oxygen.

The monomer mixture was a 92.5/7.5 w/w blend of DCPD (commercial grade 97% purity) and eth-ylidene norbornene (ENB); a solution with a freez-ing point below that of DCPD (34°C) that simplifies handling. The catalyst (0.1 N) was dissolved in one portion of the monomer mixture and the cocatalyst (0.5 M) in a second portion. A 200 mL aliquot of the cocatalyst/monomer solution was introduced into a 12 ounce beverage bottle. A 10 mL aliquot of the catalyst/monomer solution was added. After shak-ing, the reaction solution was injected by cannula into a mold 17.8 × 17.8 × 0.635 cm at 60°C. Within 30 s there ensued a rapid exotherm that peaked at about 200–210°C. After cooling, the resulting plaque was removed from the mold and prepared for the various measurements. In the experiments where toluene was deliberately added, the total amount of toluene (1.5–4.5 wt % on monomer) was added to the catalyst/monomer solution prior to mixing with the cocatalyst/monomer solution. The toluene level was found to have no effect on either the rate of reaction or on the magnitude of the reaction exo-therm.

RESULTS AND DISCUSSION

DCPD Soluble Iso- and Heteropolymetallates

We have developed two classes of compounds to re-place the tungsten and molybdenum halides tradi-tionally used with alkylaluminum compounds to ef-fect the ring-opening polymerization of DCPD. They are organoisopoly- and organoheteropolymetallates. An important advantage of these organometallates is that they can be synthesized to be highly soluble in DCPD, and yet remain unreactive toward DCPD and other norbornene type monomers under ambi-ent conditions, thus effectively eliminating the sol-ubility and shelf-life problems associated with the use of group 6 transition metal halides.

The most effective organometallates are the long-chain, trialkylammonium molybdates and tungs-tates. The isopolymetallates are typified by the $[Mo_8O_{26}]^{4-}$ anion. As described by Pope[21] the oc-tamolybdate anion occurs in two well-defined iso-meric geometries, designated as α and β. The more common β-form, is almost exclusively formed during the synthesis of isopolyoctamolybdates from water or aqueous/organic solvent systems. Figure 1 shows the structure of the $[\beta\text{-}Mo_8O_{26}]^{4-}$ isomer including a polyhedral representation. The representation clearly shows that the octamolybdate consists of eight, highly distorted molybdenum–oxygen octa-

hedra linked by bridging Mo—O—Mo interac-tions. A more detailed description of the β-octa-molybdate anion, and how it typically interacts with amine cations to form stable organomolybdate com-plexes is provided in a paper by Kroenke et al. that describes the structure of melaminium β-octamo-lybdate.[22]

In order to ensure solubility of the organometal-late component in DCPD and similar RIM mono-mers, the organocounterion needs to be chosen such that the anionic charge of the metallate is well shielded from the nonpolar medium. One such counterion that fulfills this requirement is a tertiary organoammonium cation in which the total number of carbon atoms in the alkyl chains exceeds about 30. In principle, any counterion with sufficient or-ganic character should effect solubility.

Synthesis and Characterization of Organoisopolymolybdates

The synthesis of tertiary organoammonium octa-molybdates is straightforward using a patented BF Goodrich process.[19] For example, reaction 1 illus-trates the preparation of tris[(tridecyl)ammonium] β-octamolybdate, a RIM catalyst component soluble in DCPD. Refluxing ammonium dimolybdate in acidic water with tri(tridecyl)amine in cyclohexane results in a yellow-green cyclohexane solution.

$$4[NH_4]_2[Mo_2O_7] + 4N(C_{13}H_{27})_3 + 8HCl \rightarrow$$
$$[HN(C_{13}H_{27})_3]_4[Mo_8O_{26}] + 8NH_4Cl + 2H_2O. \quad (1)$$
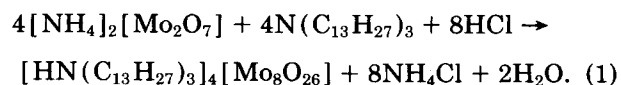
After the cyclohexane solution is separated from the aqueous phase, washed with water, and dried, re-moval of the solvent from the decanted solution iso-lates the octamolybdate procatalyst as a resinous yellow-green solid.

The organoisopolymolybdates can be readily characterized using elemental analysis, infrared spectroscopy, and powder X-ray diffraction as de-scribed in a paper that covers the synthesis and characterization of a series of melaminium isopoly-molybdates containing different isopolymolybdate anions.[23]

### Synthesis and Characterization of Organoheteropolymetallates

The heteropolymetallate anions that were found to be effective ROMP catalyst components[24] include, but are not limited to:

		MIXED
TUNGSTATES	MOLYBDATES	METALLATES
$[PW_{12}O_{40}]^{3-}$	$[PMo_{12}O_{40}]^{3-}$	$[PV_2Mo_{10}O_4]^{5-}$
$[SiW_{12}O_{40}]^{4-}$	$[P_2Mo_{18}O_{40}]^{6-}$	$[PMo_6W_6O_{40}]^{3-}$
$[BW_{12}O_{40}]^{5-}$		

Here the heteropolymetallate discussion will be limited to the details of the synthesis and characterization of the phospho-, silico-, and borotungstate Keggin[25] ions: $[PW_{12}O_{40}]^{3-}$; $[SiW_{12}O_{40}]^{4-}$; and $[BW_{12}O_{40}]^{5-}$.

The synthesis of the hydrocarbon soluble heteropolymetallates is most easily effected starting from the free acids. The phospho- and silicotungstic acids are available commercially, while the borotungstic acid was synthesized (see Experimental Section for details). Reaction of the free acids with a suitable

base such as a long-chain tertiary amine yields the hydrocarbon-soluble heteropolymetallate, as illustrated in eq. (2) for the synthesis from phosphotungstic acid. The organoammonium phosphotungstates

$$H_3[PW_{12}O_{40}] \cdot xH_2O + 3NR_3 \xrightarrow[\text{toluene}]{\text{H}_2\text{O/HCl}}$$

$$[HNR_3]_3[PW_{12}O_{40}] \quad (2)$$
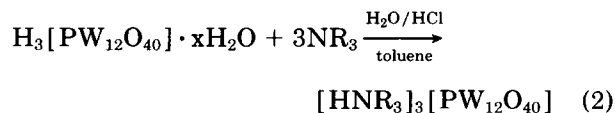
were synthesized using the previously described BF Goodrich patented two-phase reaction medium process to facilitate isolation, separation, and purification of the metallate products. The same procedure was used to prepare the silico- and borotungstates. Details of the synthesis of the phospho-, silico-, and borotungstates are given in the Experimental Section.
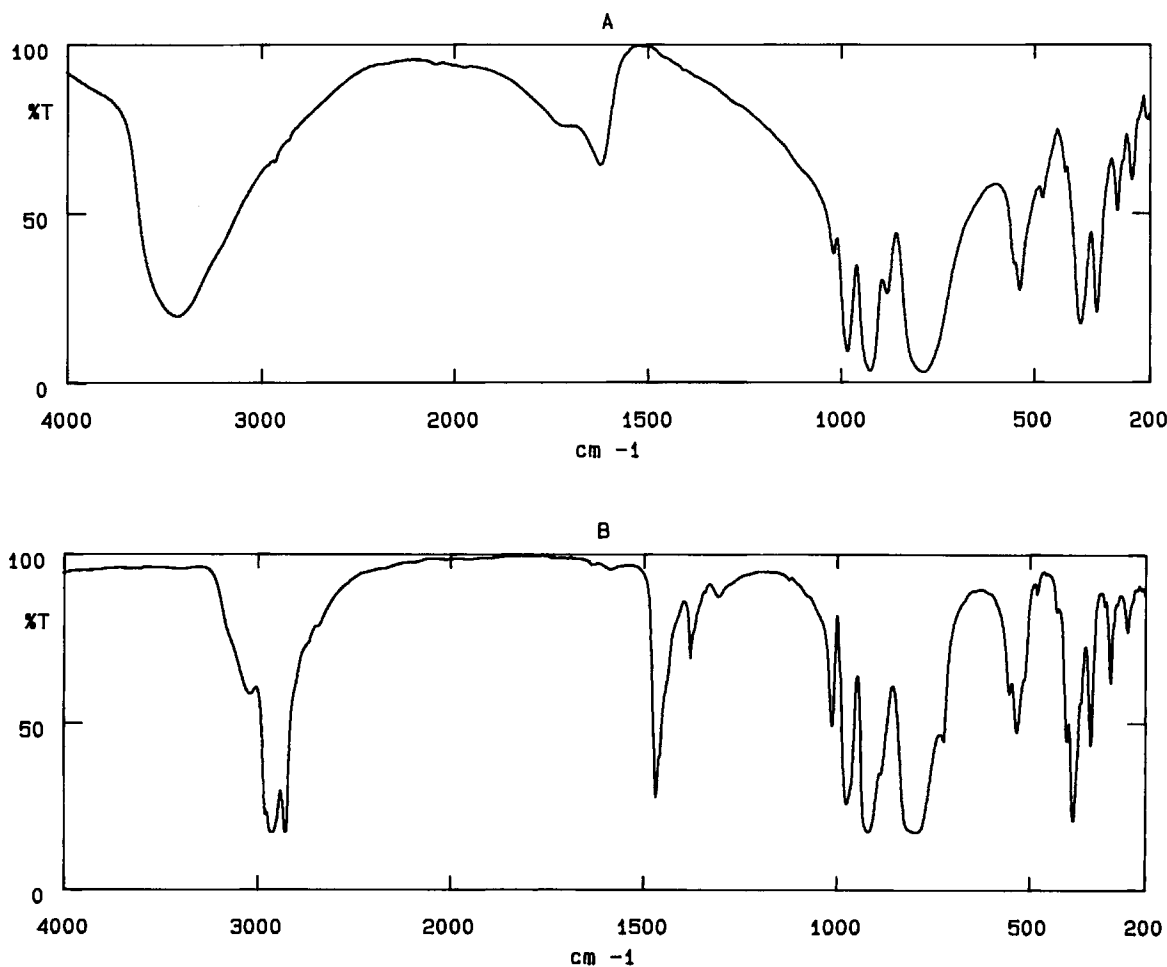

Figure 2 Infra-red spectra of (a) $H_4[SiW_{12}O_{40}] \cdot xH_2O$ and (b) $[HNR_3]_4[SiW_{12}O_{40}]$.

The organoammonium heteropolymetallates were characterized by IR spectroscopy. Figure 2 shows the IR spectra of the silicotungstic acid and a corresponding tertiary organoammonium salt. There are several features of the spectra that are notable. The high-energy, broad band at ca. 3400 cm^{-1}, assigned to the O — H stretch of water in the free acid, is no longer present in the tertiary organoammonium salt. The product does not contain water, an important consideration when alkylaluminum cocatalysts are added to the RIM formulation. The vibrations due to the tertiary organoammonium cation appear in the regions 3200–2800 cm^{-1} and 1550–1350 cm^{-1}. The remaining bands in the two spectra are remarkably similar. This suggests that the anions in the free acid and the organoammonium product have similar structures. Under the reaction conditions employed, no vast structural changes occurred in the silicotungstate starting material. The infrared bands of the heteropolytungstates synthesized to date agree with those assigned to the α-isomer.[21] These bands, especially those between 1050–700 cm^{-1}, result from various terminal W — O and bridging W — O — W vibrations.[26]

Figure 3 shows the structure and a polyhedral representation of the α-isomer of [PW$_{12}$O$_{40}$]$^{3-}$.[27] It is clear that the α-isomer consists of tungsten-oxygen octahedra linked by μ-oxygen interactions, with the phosphorus heteroatom residing at the center of the anion. The α-Keggin ion can be broken down conceptually into four metal–oxygen containing trimeric subunits. The units are assembled to maintain tetrahedral symmetry around the heteroatom. Rotation of one trimeric unit by 60° along the threefold axis of the Keggin ion would yield the corresponding β-isomer.[21]

Solubility and Stability of Tertiary Ammonium Metallates

Hydrogen bond formation between the amine cations and the nonbridging oxygen atoms in the isopolymolybdate anions stabilizes the so-called amine isopolymolybdates, including the tertiary ammonium isopolymolybdates. This extensive hydrogen bonding is most graphically illustrated in the crystal structure of melaminium β-octamolybdate, and accounts for its very high decomposition temperature, > 260°C in air.[22] An extensive literature study of hydrogen bonding in amine isopolymolybdates and tungstates suggests that hydrogen bonding plays a critical role in determining the formation, thermal

stability, and solubility of isopolymetallates and the closely related heteropolymetallates.

In the specific case of the tertiary ammonium metallates, the polarized N — H bond is expected to attach itself to the metallate ions through the formation of hydrogen bonds with the terminal, nonbridging oxygens. This interaction will effectively orient the alkyl chains away from the source of anionic charge, that is, the surface of the large metallate anions. In this manner, the ammonium cation acts as a "surfactant" and effectively shields the charge. The complex thus appears as a large organic molecule to surrounding solvent molecules. Addition of increasingly longer alkyl chains allows for solubility of the metallates in increasingly apolar organic media.

The ability to prepare molybdenum and tungsten metallate catalysts that are soluble in DCPD (and other suitable monomers) and stable to air and moisture under ambient conditions simplifies and facilitates the conduct of the RIM polymerization process. In contrast, when using traditional molybdenum and tungsten RIM catalysts, such as WCl$_6$, their insolubility in monomer, and reactivity with water, necessitates preparing the catalyst solutions in rigorously dried solvents, such as toluene. The use of a reaction solvent, such as toluene, is undesirable. For example, residual toluene in the final RIM product adversely effects the polymer properties as illustrated in the following.

Effect of Residual Process Solvent on Polymer Properties

In the majority of polymerization processes (either batch or continuous) the use of a reaction solvent affects only the operation of the process itself; the product polymer normally being dried under vacuum to reduce residual solvent levels to the ppm level. However, in the case of RIM, all components in the reactant stream(s) (including catalyst and solvent) are present in the final part.

We find that simple hydrocarbon solvents such as toluene, and even unconverted monomer, are very effective plasticizers for the RIM DCPD thermoset products. The excellent solvent resistance of these thermosets further compounds the retention of the reaction solvent by impeding the diffusion of the hydrocarbon from the final thermoset product. The unwanted result is a permanently plasticized thermoset product. The effect of low levels of incorpo-
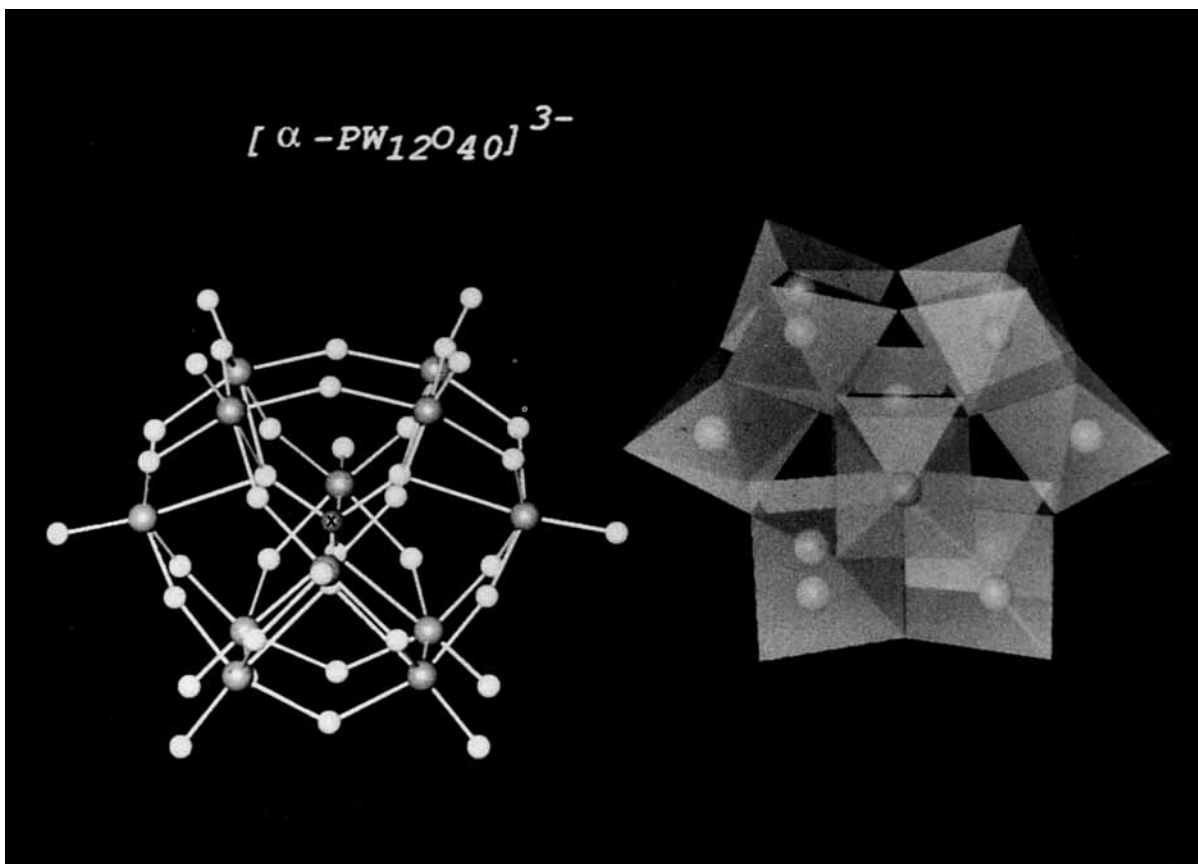
Figure 3   Structure and polyhedral representation of $[PW_{12}O_{40}]^{3-}$ (crystallographic data from reference 27). The large dark spheres represent tungsten, the small white spheres oxygen, and the x'ed sphere phosphorus.
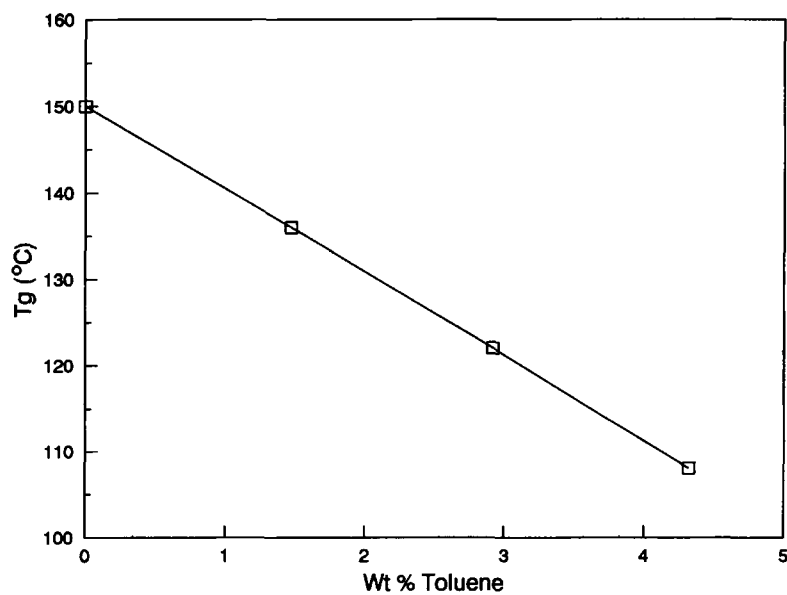
Figure 4   Glass transition temperature (as measured by dynamic mechanical spectroscopy) of dicyclopentadiene-ethylidene norbornene copolymer as a function of added toluene.
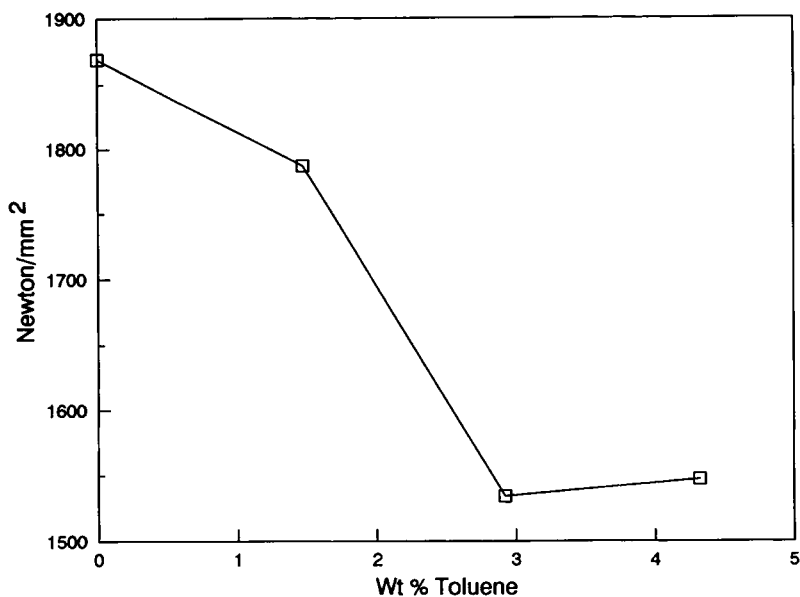
Figure 5   Flexural modulus of dicyclopentadiene-ethylidene norbornene copolymer as a function of added toluene.

rated toluene on product performance is illustrated in Figures 4–6.

Figure 4 shows that the use of toluene as a diluent reduces the T_g (glass transition temperature) by about 10°C for every 1 wt % of toluene incorporated (the commercially important heat distortion temperature is affected similarly). Several patent examples and the studies of Macosko et al.[28] show that

approximately 3 wt % toluene (on total formulation) is required to dissolve the tungsten halide catalyst; hence the glass transition temperature of the final part will be diminished by about 30°C. Indeed, Macosko reported T_g's of 119–125°C compared to the 150°C observed with our solvent-free system. Figure 5 shows that the flexural modulus behavior of DCPD resins with and without incorporated toluene par-
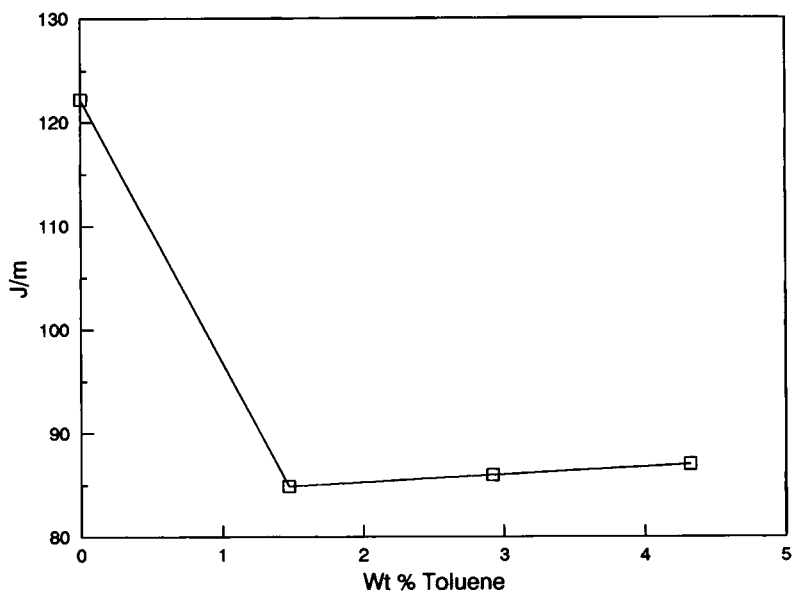
Figure 6   Notched Izod impact strength of dicyclopentadiene-ethylidene norbornene copolymer as a function of added toluene.

allels the effect observed on T_g; increasing levels of solvent result in a sizeable reduction in the stiffness of the polymer. The impact properties of the material did not show a first order relationship with the level of incorporated solvent. Furthermore, there was clearly no gain in impact strength to compensate for the loss in flexural modulus as a result of residual toluene (Fig. 6).

Product Advantages

Besides polymers with higher T_g and flexural modulus, other advantages of these new metallate catalyst systems include high conversion and halogen-free formulations.

Compared with the more conventional tungsten chloride-based systems, conversions of 97–98% are routinely obtained using commercial "pure" DCPD monomer, with an actual DCPD content of about 97%. This is reflected in higher glass transition temperatures and lower residual monomer contents (and possible odor problems).

Using these metallate catalysts in combination with new cocatalyst systems we are able to achieve high conversions (in excess of 95%) in the total absence of halide ion. This has important ramifications in application areas such as electronics.

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