

End-Grafting of Oligoesters Based on Terephthalic Acid and Linear Diols for High Solids Coatings

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SYNOPSIS

Oligomers derived from terephthalic acid and 1,6-hexanediol or 1,10-decanediol have been chemically modified through end-grafting with succinic anhydride or trimellitic anhydride followed by glycidyl neodecanoate. The grafted oligomers are paste-like semisolids or viscous liquids at room temperature. As the grafted oligomers are heated, their viscosity goes down to a minimum, then up to a maximum, and then down again. Combined DSC, crossed polarizing microscopy, and wide-angle x-ray diffraction indicate that the grafted oligomers form crystalline domains dispersed in amorphous phase. The grafted oligomers are soluble in common organic solvents, such as toluene, at lower concentrations (<14–51 wt %) and form stable dispersions at higher concentrations. High solid coatings formulated with melamine or isocyanate resins gave glossy films with excellent combined hardness and impact resistance. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Localized self-assembly of polymer segments through formation of crystalline domains can enhance the hardness and impact resistance of the material by acting as reversible crosslinking sites. Under impact, the self-assembled polymer segments can absorb energy by shifting positions within an assembly or by reversibly breaking and re-forming, avoiding macroscopic damages. The widely used tough polymers polyurethanes are examples of polymers with localized crystalline domains or aggregates, consisting of the hard segments dispersed among the amorphous phase, primarily consisting of the soft segments.¹

Polyesters based on terephthalic acid and linear diols are highly crystalline because of the rigidity and symmetry of the terephthalate units. In fact, both the high and low molecular weight polyesters based on terephthalic acid and linear diols are insoluble in common organic solvents apparently be-

cause of their strong tendency to form crystals. While the strong crystal-forming tendency of polyesters or oligoesters based on terephthalic acid and linear diols makes it difficult to use them in liquid coatings because of the insolubility and opaqueness, such a tendency may be useful in designing coatings capable of localized self-assembly of segments. Patents^{2–4} indicate that powder coatings containing oligoesters based on terephthalic acid and linear diols can give excellent mechanical properties. We recently reported that nonaqueous dispersion coatings based on oligoester of terephthalic acid and 1,6-hexanediol exhibit excellent combined hardness and impact resistance, in addition to strong thixotropic behavior and excellent sagging resistance.⁵

In this article we report the terminal grafting of oligoesters based on terephthalic acid and linear diols (average degree of polymerization, mean = 2) to make them usable as crosslinkable components of solvent-borne coatings. Two linear diols, 1,6-hexanediol and 1,10-decanediol, were chosen for the studies because of their wide commercial availability. The oligoesters were first grafted with succinic anhydride or trimellitic anhydride, followed by glycidyl neodecanoate, as illustrated in Schemes I and II. The grafted oligomers have soft terminal units and

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partially rigid central units with a regular alternating structure. It was expected that such terminal grafting would promote the solubility and dispersibility of the oligoesters, and it was hoped that localized crystallization or self-assembly of the terephthalate units could still enhance hardness and toughness of crosslinked films.

EXPERIMENTAL SECTION

Materials

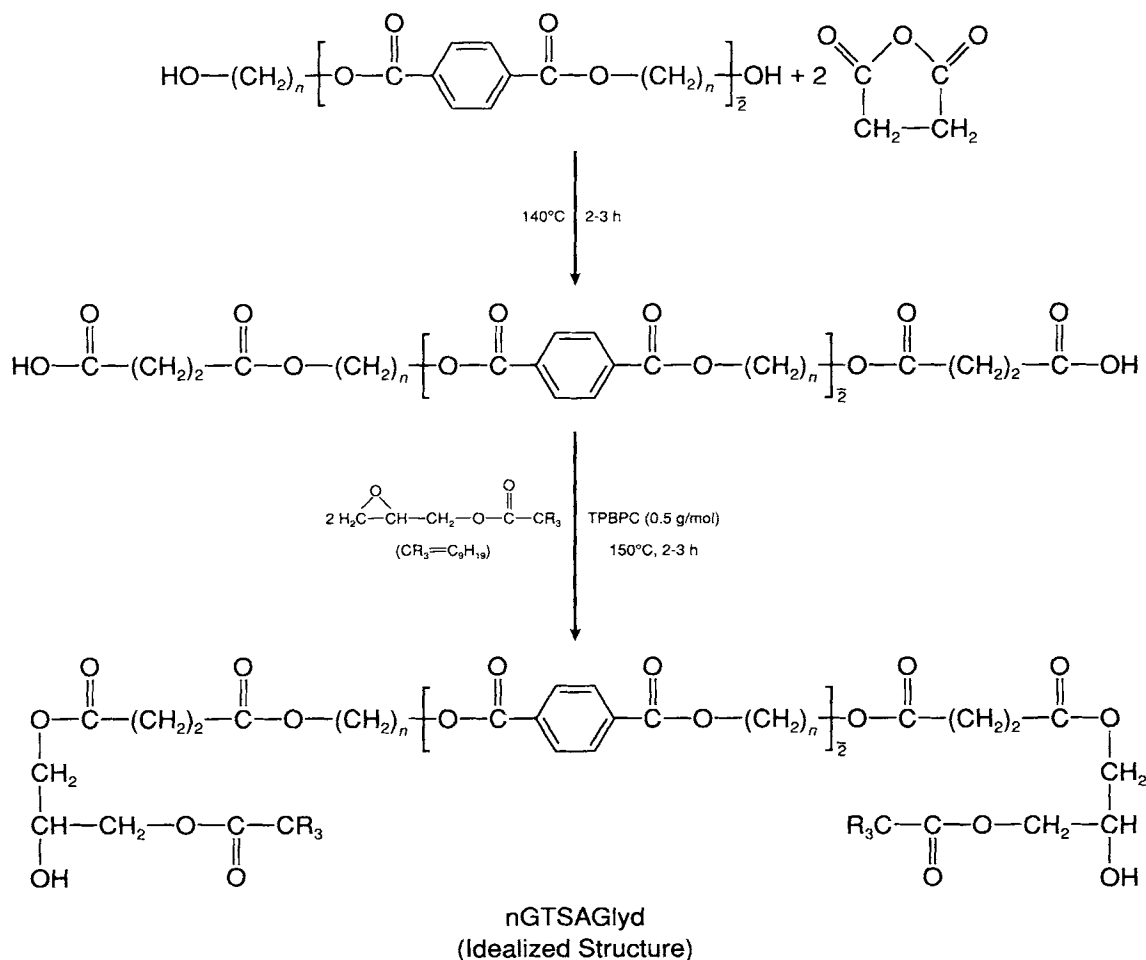
Glycidyl neodecanoate was obtained from the Exxon Chemical Company under the trade name Glydext N-10. Hexakis (methoxymethyl) melamine resin (Resimene 746, HMMM) and isocyanate resin (Mondur CB-60, mixed trimers of 2,4-toluenediisocyanate, TIC) were obtained from Monsanto Chemical Company and Miles Corporation, respectively.

Elvacite AB-1040 (AB dispersant, 40 wt % solution) and Tipure R-960 (TiO_2) were obtained from Du Pont. Byk-020 (defoamer) was obtained from Byk Chemie. All other chemicals were purchased from the Aldrich Chemical Company. For coatings formulated with isocyanate resin, the solvent was dried over molecular sieves before use; all other materials were used as received.

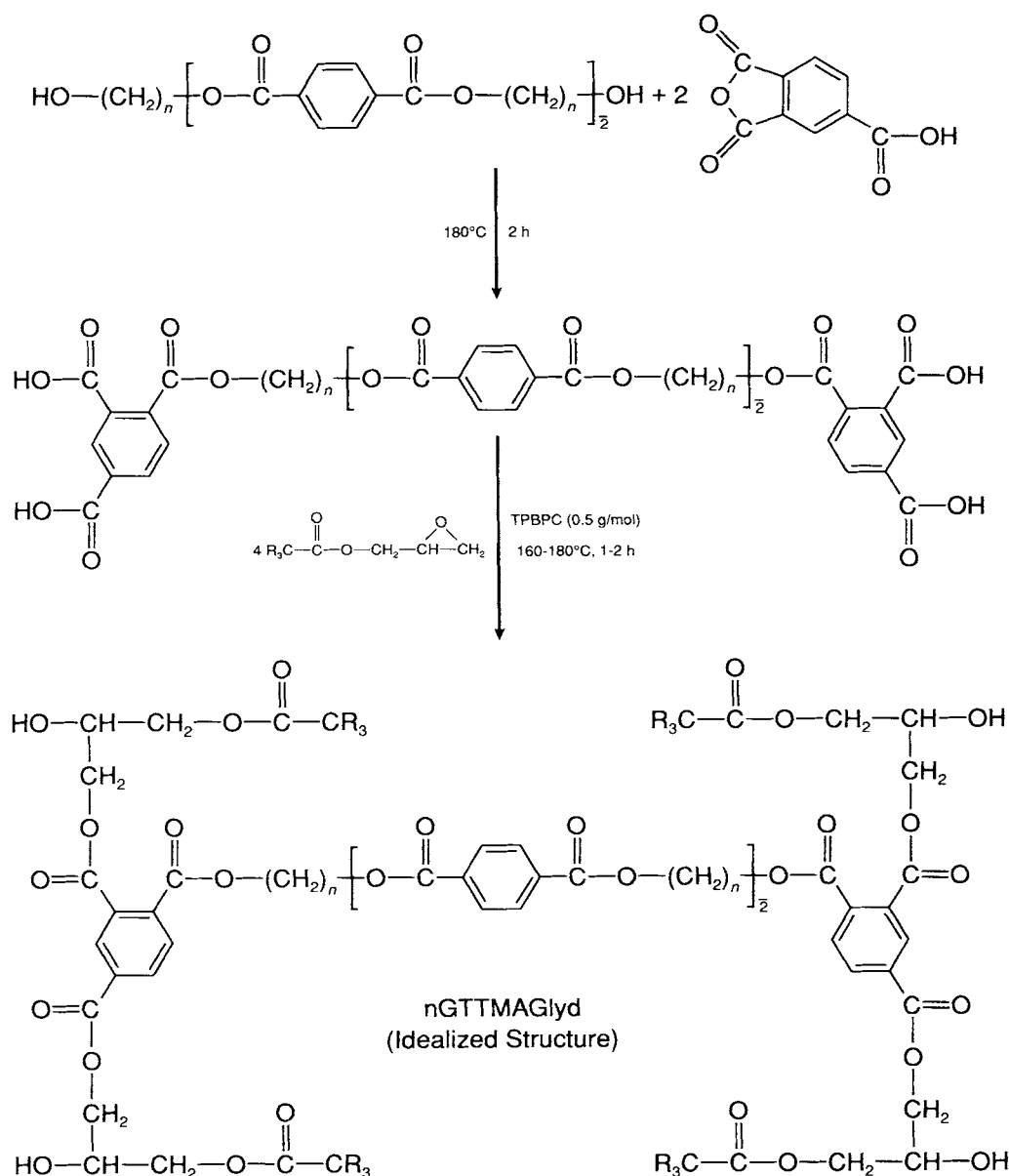
Oligoester Syntheses and Terminal Graftings

nGT

The oligoesters 6GT and 10GT were synthesized through melt esterification from dimethyl terephthalate and 1,6-hexanediol or 1,10-decanediol (2:3 mol ratio) with zinc acetate dihydrate (0.2% of total weight) as a catalyst. The synthetic procedure was described in our earlier report.⁵



Scheme I.



Scheme II.

The 6GTSAGlyd Oligomer

6GT (61.5 g, 0.10 mol) and succinic anhydride (20.0 g, 0.20 mol) were charged into a 250 mL round-bottom flask equipped with a stirrer and thermometer. The materials were heated to 140°C in about 1 h and kept at this temperature until the reaction was complete (in about 2 h). The completeness of the reaction was monitored by NMR spectroscopy [for 6GTSA oligomer, NMR: 1.2–1.8 (very strong, —CH₂—), 2.6 (medium, —CH₂—CO—O—), 4.3 (medium, —CH₂—O—CO—), 8.1 (medium, ben-

zene ring)]. Into the above intermediate, glycidyl neodecanoate (55 g, 0.22 mol, 10% excess) and triphenyl benzyl phosphonium chloride (TPBPC, 0.11 g) were added. The temperature was raised to about 150°C and maintained there for 2 to 3 h. The hot material was dissolved in 500 mL of toluene in a 1000 mL beaker. It was kept at room temperature for 5 h to let any insoluble oligomer (such as unreacted nGT, if any) precipitate. Generally, no precipitate was found. The solution (soluble part) was concentrated on a rotary evaporator and then mixed with 400 mL of petroleum ether. Because

glycidyl neodecanoate is soluble in petroleum ether but the grafted oligomer is not, the grafted oligomer separated to the bottom as viscous liquid. The petroleum ether solution was decanted, and the viscous liquid was washed with two additional portions of petroleum ether. The viscous liquid was dried under vacuum at 80°C overnight, yielding 117 g (89%) of the product, which is a milky-white opaque, paste-like, semisolid. NMR spectroscopy was consistent with the expected oligomer structure [0.85 (strong, $-\text{CH}_3$), 1.2–1.8 (very strong, $-\text{CH}_2-$), 2.6 (strong, $-\text{CH}_2-\text{COO}-$ on succinate group), 3.7 (weak, $-\text{CH}_2-\text{OH}$ or $\text{R}_2\text{CH}-\text{OH}$), 4.0–4.4 (strong, $-\text{CH}_2-\text{O}-\text{CO}-$), 8.1 (strong, aromatic ring)].

The 10GTSAGlyd, 6GTTMAGlyd, and 10GTTMAGlyd Oligomers

Similar procedures as for 6GTSAGlyd were used. The grafted oligomer 10GTSAGlyd was milky-white, opaque, paste-like semisolid, and 6GTTMAGlyd and 10GTTMAGlyd were milky-white, opaque, viscous liquids.

The 6GPTMAGlyd Oligomer

This oligomer has the same structure as 6GTTMAGlyd except that the terephthalate moiety is replaced with the phthalate moiety. The 6GPTMAGlyd oligomer was synthesized by a method similar to that for 6GTTMAGlyd except that phthalic anhydride was used instead of dimethyl terephthalate. Phthalic anhydride and 1,6-hexanediol (2:3 mol ratio) first polymerized (melt-esterification) to form oligoester diol (6GP). The oligoester diol 6GP was further end-grafted with trimellitic anhydride and then glycidyl neodecanoate to form 6GPTMAGlyd. Same purification procedures as for 6GTSAGlyd were carried out. The final product 6GPTMAGlyd was light-yellow, transparent, paste-like semisolid.

Determination of Solubility and Limiting Concentration of Dispersion

The grafted oligomers had appreciable, but limited, solubility in organic solvents. At levels exceeding the upper limit of solubility but below the limiting concentration of the dispersion, they form self stabilizing nonaqueous dispersions.

Solubility

The oligomer (more than the amount needed for the saturated solution, such as 10 g) was dissolved in

the solvent (such as 10 g) with heating and stirring. After cooling down to room temperature, dispersion usually formed. Additional solvent was added slowly with stirring until the dispersion changed to clear solution. The solubility (wt %) was calculated from the total amounts of oligomer and the solvent.

Limiting Concentration of Dispersion

The limiting concentration of dispersion (LCD) was defined as the maximum percent solids of the dispersion at which the material remains free-flowing liquid at room temperature. Here, free-flowing liquid is defined as one that can be poured out of a 250 mL beaker within seconds. Above LCD, the materials become paste-like semisolid (nGTSAGlyd) or viscous liquid (nGTTMAGlyd).

Formulation of Coatings

Clear Coatings

The oligomer (1.4 g) and xylene (1.0 g) were charged into a 10 mL vial and heated over a steam bath until the oligomer dissolved. The vial was taken away from the steam bath and, after the temperature of the vial dropped to about 50°C, HMMM (0.6 g) and *p*-toluenesulfonic acid monohydrate (*p*-TSA, 0.004 g) were added. The vial was rapidly swirled by hand in the room temperature air until the material reached room temperature. A stable dispersion formed. For ungrafted oligomer, chloroform instead of xylene was used as solvent to form transparent coating solutions.

For coatings with isocyanate resin (TIC) as a crosslinker, the above procedure was used except that 1.1 equivalent of isocyanate relative to 1.0 equivalent of hydroxy functional oligomer was used with dibutyltin dilaurate (0.05% by weight based on the total resins) as a catalyst.

Pigmented Coatings

For pigmented coatings, the percent solids (60%) and the weight ratios of the resins to the catalyst were the same as for clear coatings. However, TiO_2 pigment in an amount of about 40% based on total solids weight was added together with Elvacite AB-1040 (3% Elvacite AB-1040 solution based on pigment weight) as dispersant and two drops of Byk-020 as defoamer (for 100 g of formulation).

In a typical formulation, the oligomer was first dissolved in xylene with heating over a steam bath, and after cooling to near room temperature, HMMM

Table I Limiting Solubility (LS)^a and Limiting Concentration of Dispersion (LCD)^b of the Glycidyl Neodecanoate Grafted Oligomers at Room Temperature (wt %)

| Modified Oligomers | Toluene | | Xylene | | MIBK | |
|--------------------|---------|-----|--------|-----|------|-----|
| | LS | LCD | LS | LCD | LS | LCD |
| 10GTSAGlyd | 23 | 72 | 15 | 67 | 16 | 70 |
| 6GTSAGlyd | 22 | 75 | 15 | 70 | 14 | 75 |
| 10GTTMAGlyd | 48 | 75 | 42 | 70 | — | — |
| 6GTTMAGlyd | 51 | 80 | 46 | 75 | — | — |

^a LS is the highest concentration at which a clear solution forms at room temperature.

^b LCD is the highest concentration at which the dispersion remains free-flowing liquid at room temperature.

and *p*-TSA were added with stirring, followed by pigment, dispersant, and defoamer. The coating was dispersed in a high-speed dispersing mill until the Hegmann grind reached 7 N.S. (in about 30 min). The container and the coating were weighed before dispersing and the solvent lost during dispersing was replenished.

Film Formation

Each coating was cast on a treated steel panel (Bonderite 1000) using a Meyer rod. The coatings formulated with melamine resin were baked at 150°C in an oven for 30 min, and the coatings formulated with the isocyanate resin were cured at 70°C for 2 h.

Instrumental Methods

Differential scanning calorimetry (DSC), wide-angle x-ray diffraction (WAXD), crossed polarizing microscopy, ICI viscosity, and NMR spectroscopy were measured as described.⁵

Tests of Film Properties

The film properties were tested 1 day after cross-linking. Pencil hardness, Knoop hardness, reverse impact resistance, and crosshatch adhesion were measured according to ASTM D3363, D1474, D2794, and D3359,⁶ respectively. Resistance to MEK was recorded as the minimum times of double rubs required to scratch through the coatings by rubbing a piece of cloth saturated with methyl ethyl ketone (MEK). The appearance of the film was determined by visual evaluation. Film thickness was measured by a magnetic thickness apparatus. Dry thickness was 25–30 μm.

RESULTS

Solubility and Dispersibility

Table I shows the solubilities of the grafted oligomers in toluene, xylene, and methylisobutylketone (MIBK), respectively, in terms of wt %. All of the glycidyl neodecanoate grafted oligomers form clear solutions in toluene, xylene, and MIBK up to a certain concentration (14–51 wt %). At higher concentrations, they form stable, nonaqueous dispersions that are free flowing at concentrations up to 67–80 wt %. In contrast, the ungrafted oligomers are essentially insoluble in these solvents at room temperature. In chloroform, both the ungrafted and grafted oligomers are very soluble.

Morphology of the Grafted Oligomers

*n*GT Oligomers Bifunctionally Grafted with Glycidyl Neodecanoate (*n*GTSAGlyd)

Both 6GTSAGlyd and 10GTSAGlyd were milky-white, opaque, paste-like semisolids at room temperature. At slightly higher temperature (above 30–40°C), they became turbid liquids. The DSC thermographs of both oligomers showed two transitions on heating (40 and 76°C for 6GTSAGlyd, and 29 and 70°C for 10GTSAGlyd) and one transition above 40°C on cooling (54°C for 6GTSAGlyd and 50°C for 10GTSAGlyd) (The DSC data below 40°C for cooling were not measured because of instrument limitation.). A typical DSC trace is shown in Figure 1 (for 10GTSAGlyd). The lower transitions on heating appear to be second order (glass transition). The higher transitions on heating and the transitions on cooling occur when the oligomers change between turbid and clear liquids.

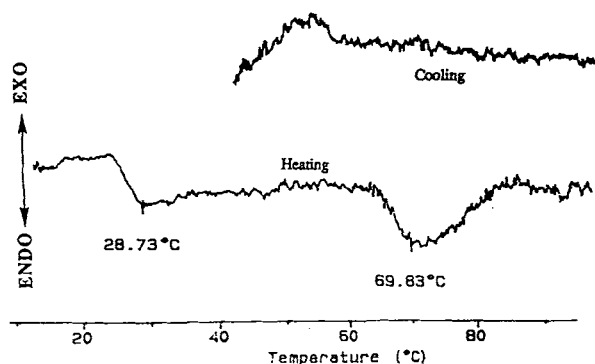


Figure 1 DSC thermograph of 10GTSAGlyd; both the heating and the cooling rates were 3°C/min.

Melting of crystalline particles dispersed in the liquid phase may be attributed to these first order transitions.

The crossed polarizing micrographs of both 10GTSAGlyd and 6GTSAGlyd at room temperature exhibit grain-like textures, as shown in Figure 2 for 10GTSAGlyd, indicating the presence of crystalline domains. WAXD pattern of 6GTSAGlyd at room temperature shows two strong peaks at 20.1° (4.40 Å) and 20.7° (4.27 Å), together with several weak peaks and a broad halo, as shown in Figure 3, indicating the presence of both crystalline and amorphous domains.

nGT Oligomers Tetrafunctionally Grafted with Glycidyl Neodecanoate (*nGTTMAGlyd*)

Both 6GTTMAGlyd and 10GTTMAGlyd were milky-white, opaque, viscous liquids at room temperature. DSC (heating curve) shows two first order transitions at 15 and 52°C for 10GTTMAGlyd

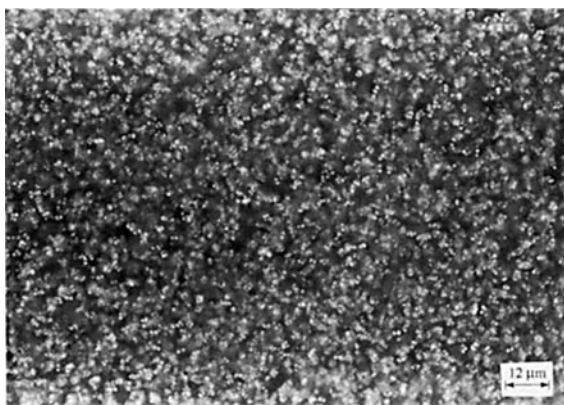


Figure 2 Crossed polarizing micrograph of 10GTSAGlyd at room temperature.

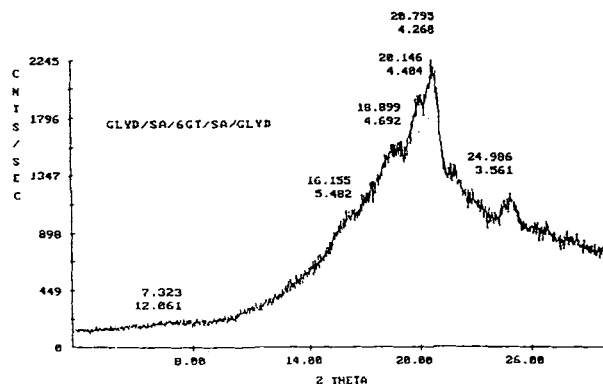


Figure 3 WAXD pattern of 6GTSAGlyd at room temperature.

and three transitions at 3, 43, and 59°C for 6GTTMAGlyd (as shown in Fig. 4 for 6GTTMAGlyd), indicating phase transitions at these temperatures. Crossed polarizing micrographs of both oligomers at room temperature exhibit scattered grains (Fig. 5 for 10GTTMAGlyd), suggesting the presence of crystalline particles suspended in the amorphous phase. WAXD patterns of both 6GTTMAGlyd and 10GTTMAGlyd exhibit a strong broad halo in the higher angle region, as shown in Figure 6 for 6GTTMAGlyd. The broad halo is attributable to amorphous glass. The absence of strong peaks in the wide angle region suggests that the total volume of crystalline domains is small.

Rheological Properties of the Modified Oligomers

Table II shows the ICI viscosity vs. the temperature of 6GTSAGlyd, 6GTTMAGlyd, and 10GTTMAGlyd. The oligomer exhibits a viscosity minimum, and

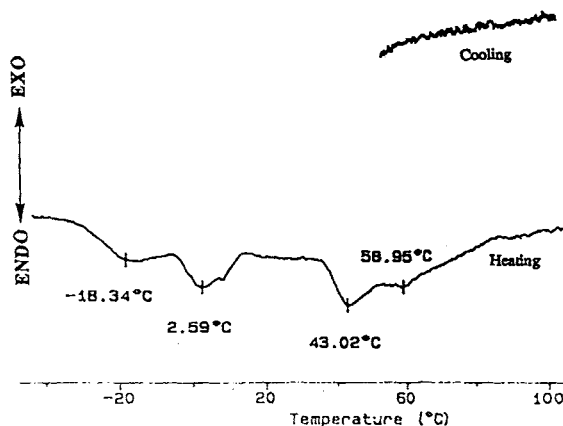
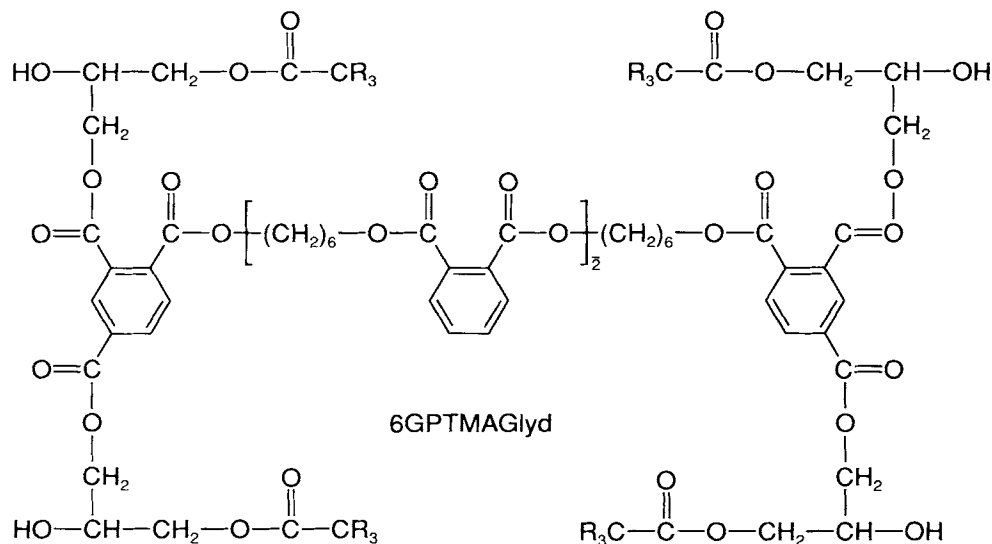


Figure 4 DSC thermograph of 6GTTMAGlyd; both the heating and the cooling rates were 3°C/min.

then a maximum, during heating, and the same phenomenon was seen during cooling. The minimum and maximum are in the range of the two transitions determined by DSC.

For comparison, a noncrystalline oligomer (6GPTMAGlyd) with structure similar to 6GTTMAGlyd was studied by the ICI viscometer. This oligomer was transparent in both solid and liquid states, in-

dicating that it is an amorphous glass or liquid, depending on temperature. As shown in Table II, with increasing temperature, the ICI viscosity of the 6GPTMAGlyd oligomer decreases after 75°C (the viscosity below 75°C is too high to be determined by the ICI viscometer). No viscosity minimum or maximum is observed, in contrast to 6GTTMAGlyd oligomer.



Film Properties

Table III shows the properties of the coatings based on the grafted oligomers and HMMM or TIC resin. It is seen that the coatings based on glycidyl neodecanoate-grafted oligomers and melamine resin exhibit good hardness and excellent reverse impact resistance, adhesion, solvent resistance, and transparent appearance. As expected, the grafted oligomers gave somewhat less hard coatings than the ungrafted ones, apparently due to the incorporation of flexible grafts. However, the grafting changed the coating appearance from hazy to transparent/glossy, possibly due to the improved compatibility of the grafted oligomers with the crosslinkers during curing; such transparent/glossy appearance is essential for most coating applications.

Morphology of Coatings Based on Grafted Oligoesters

Figure 7 shows the WAXD of 10GTSAGlyd cross-linked with HMMM. A strong broad halo in the higher angle region and some weak diffraction peaks are seen. The strong broad halo may be attributable

to amorphous glass. The weak peaks in the higher angle region indicate the presence of a small amount of crystalline domains. The weak but sharp peak in the lower angle region suggests the presence of layer structures. Therefore, the oligomers mainly consist of amorphous glass, together with a small amount of crystalline domains. The presence of crystalline domains is further confirmed with the crossed polarizing micrograph of 10GTSAGlyd (Fig. 8), which shows scattered grains. The concentration of the crystalline domains in crosslinked coatings is much lower than in the grafted oligomers alone, possibly because formulating with the melamine resin reduces the concentration of self-assembly units, and the crosslinking restricts such units from assembling with one another.

DISCUSSION

Morphology of Grafted Oligomers

The above results indicate that the grafted oligomers nGTSAGlyd and nGTTMAGlyd are paste-like semisolid and viscous liquid, respectively, at

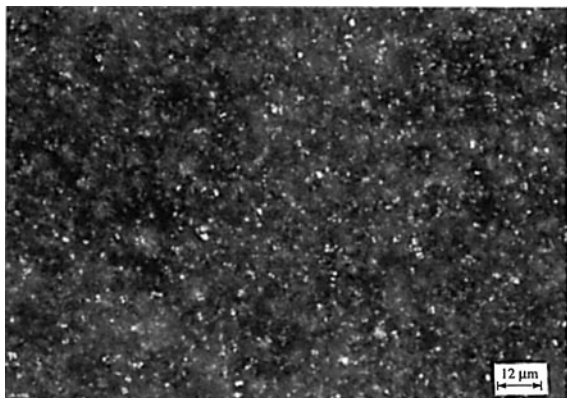


Figure 5 Crossed polarizing micrograph of 10GTTMAGlyd at room temperature.

room temperature, both consisting of crystalline domains dispersed in the amorphous phase. Such a result may be explained as follows. Because the ungrafted oligoester nGT (average degree of polymerization, mean = 2) was synthesized through melt transesterification, it consists of molecules with different degrees of polymerization (DP). While the average DP is 2, there are molecules with DP lower and higher (DP = 1, 3, 4, 5, 6, . . .). The grafted oligomers will have a similar DP distribution, assuming negligible transesterification. The grafted oligomers with higher DP tend to form crystalline domains and the grafted oligomers with lower DP tend to form amorphous phase. Therefore, at room temperature, the grafted oligomers appear to consist of crystalline domains of molecules with higher DP dispersed in amorphous phase of molecules with lower DP. Because the grafted oligomers have the same end-grafts that are compatible to one another, the grafts on the surface molecules of the crystalline domains should expand to the amorphous phase, giving steric stability of the dispersed crystalline domains. The first-order transitions measured by DSC can be attributed to melting (on heating) of the crystalline domains or crystallization of the molecules with higher DP. The presence of three first-order transitions of nGTTMAGlyd can be attributed to crystalline domains of different DP.

While the experimental data point to the direction that the grafted oligomers consist of crystalline domains dispersed in the amorphous phase, some of these data may be interpreted as that the grafted oligomers contain liquid crystalline domains although such a hypothesis is unlikely because the terephthalate units are widely thought to be non-

mesogenic. Such an interpretation follows. Because the first-order transitions occur when the oligomers change from opaque paste-like semisolid to transparent liquid (for nGTSAGlyd) or from opaque, viscous liquid to transparent liquid (for nGTTMAGlyd), there is a possibility that the terephthalate moieties (which may be considered semirigid⁷) in the grafted oligomers form liquid crystalline domains above the lower transition temperature. Indeed, the crossed polarizing micrographs of the grafted oligomers (Figs. 2 and 5) showed grain-like textures, similar to those of some liquid crystalline polymers reported in the literature.⁸⁻¹¹

Unusual Rheological Behavior

The unusual rheological behavior can be explained by the above-proposed morphology that the grafted oligomers consist of crystalline domains of molecules with higher DP dispersed in amorphous phase of molecules with lower DP. The viscosity maximum may be explained by the melting of the crystalline particles consisting of higher DP molecules. The molecules melted from the particles will increase the average DP of the liquid phase and give higher viscosity. Below the viscosity minimum, the viscosity decreases with increasing temperature due to increasing mobility of the liquid phase. Above the viscosity maximum, the oligomers are in single, liquid phase, and, therefore, the viscosity decreases with increasing temperature.

As for the morphology, the presence of viscosity minimum and maximum during heating and cooling may also be explained by liquid crystalline transition, because such an unusual rheological behavior is generally observed in thermotropic LC materials.^{12,13}

Formation of Nonaqueous Dispersion

At lower concentration, the grafted oligomers are soluble in common organic solvents (such as toluene)

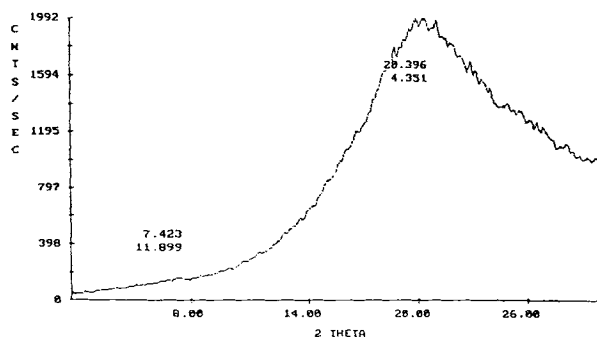


Figure 6 WAXD of 6GTTMAGlyd at room temperature.

Table II ICI Viscosity (Poise) vs. Temperature of Oligoesters

| Temperature (°C) | 25 | 50 | 75 | 100 | 125 | 150 |
|---------------------|--------------------|--------------------|--------------------|------|-----|-----|
| 6GTSAGlyd-Heating | > 100 ^a | 12.0 | 15.5 | 2.0 | 0.2 | |
| 6GTSAGlyd-Cooling | 45.0 | 2.0 | 15.2 | 2.5 | 0.1 | |
| 6GTTMAGlyd-Heating | > 100 ^a | 34.0 | > 100 ^a | 29.5 | 7.5 | 1.5 |
| 6GTTMAGlyd-Cooling | > 100 ^a | 89.0 | > 100 ^a | 36.5 | 9.0 | 1.5 |
| 10GTTMAGlyd-Heating | — | > 100 ^a | 1.5 | 0.4 | 2.5 | 1.2 |
| 10GTTMAGlyd-Cooling | — | > 100 ^a | 1.5 | 0.6 | 2.5 | 1.1 |
| 6GTPMAGlyd-Heating | > 100 ^a | > 100 ^a | > 100 ^a | 29.0 | 7.5 | 1.5 |
| 6GTPMAGlyd-Cooling | > 100 ^a | > 100 ^a | > 100 ^a | 28.0 | 5.4 | 1.8 |

^a 100 poise is the maximum viscosity value measurable with the instrument available.

at room temperature. Apparently, the grafting makes the oligomers soluble by increasing solvent-compatible components of the oligomers and by reducing the ease with which nGT units can form crystals. (The ungrafted oligomer is insoluble in these solvents at room temperature.)

At higher concentration, stable dispersion forms, apparently due to the crystallization of higher DP oligomers. The higher DP oligomers should be less

soluble than the lower DP ones and should come out of solution first as hot solution is cooled. Such higher DP oligomers should crystallize to form particles. The grafts on the surface molecules of the particles may expand to the solution phase, sterically stabilizing the dispersion. Some of the soluble, low DP oligomers may be trapped to the crystalline particles with the terephthalate moieties attached to the terephthalate moieties on the

Table III Film Properties of Coatings Based on Grafted Oligoesters^a

| Oligomer | X-Linker | Pigment | Pencil Hardness | Tukon Hardness (KHN) | Reverse Impact (in-lbs) | Appearance ^b |
|-------------------|----------|------------------|-----------------|----------------------|-------------------------|-------------------------|
| 10GTSAGlyd | HMMM | None | 3H/4H | 12 | > 160 | Tr |
| 6GTSAGlyd | HMMM | None | 4H/5H | 13 | 120 | Tr |
| 10GTTMAGlyd | HMMM | None | 3H/4H | 13 | > 160 | Tr |
| 6GTTMAGlyd | HMMM | None | 4H/5H | 14 | > 160 | Tr |
| 10GTSAGlyd | TIC | None | 4H/5H | 18 | > 160 | Tr |
| 6GTSAGlyd | TIC | None | 4H/5H | 20 | > 160 | Tr |
| 10GTTMAGlyd | TIC | None | 5H/6H | 20 | > 160 | Tr |
| 6GTTMAGlyd | TIC | None | 5H/6H | 20 | > 160 | Tr |
| 10GTSAGlyd | HMMM | TiO ₂ | 4H/5H | 14 | > 160 | Gl |
| 6GTSAGlyd | HMMM | TiO ₂ | 5H/6H | 15 | 100 | Gl |
| 10GTTMAGlyd | HMMM | TiO ₂ | 4H/5H | 14 | > 160 | Gl |
| 6GTTMAGlyd | HMMM | TiO ₂ | 5H/6H | 16 | 120 | Gl |
| 10GTSAGlyd | TIC | TiO ₂ | 4H/5H | 20 | 120 | Gl |
| 6GTSAGlyd | TIC | TiO ₂ | 5H/6H | 22 | > 160 | Gl |
| 10GTTMAGlyd | TIC | TiO ₂ | 5H/6H | 22 | > 160 | Gl |
| 6GTTMAGlyd | TIC | TiO ₂ | 6H/7H | 22 | > 160 | Gl |
| 10GT ^c | HMMM | None | 6H/7H | 20 | > 160 | Hazy |
| 10GT ^c | TIC | None | 6H/7H | 28 | > 160 | Hazy |

^a All coatings have percent solids of about 65% with xylene as solvent. For HMMM crosslinked coatings, 0.2% of p-TSA based on the resins was added. For TIC crosslinked coatings, 0.16% of dibutyltin dilaurate based on the resins was added. Pigmented coatings contain 3% of AB dispersant (40% solution) based on weight of TiO₂. All films in this table have crosshatch adhesion of 100% and MEK resistance of >100 double rubs. The coatings were cured at 150°C for 30 min with HMMM crosslinker and 70°C for 2 h with TIC crosslinker.

^b Gl means glossy and Tr means transparent.

^c Chloroform was used as solvent.

particles and the grafts extended into the solution, helping stabilizing the dispersion. The mechanism for the stabilization of such dispersions may be similar to that suggested in a nonaqueous dispersion based on insoluble crystalline oligomer and soluble dispersant.⁵ Here the higher DP oligomer molecules act as the insoluble crystalline oligomer and the lower DP oligomer molecules act as the dispersant.

As expected, higher number of grafts per oligomer gives better solubility. However, there is no significant increase in LCD with increasing number of grafts. In other words, bifunctional grafting is as efficient as tetrafunctional grafting in terms of forming stable dispersions. Although the bifunctionally grafted oligomers are less compatible with solvent compared to tetrafunctional ones, their dispersion particles may have higher solid content (containing less solvent within the particles) and leave more solvent in the liquid phase, effectively increasing solids level attainable.

CONCLUSION

Crystalline oligomeric diols can be end-grafted with succinic anhydride or trimellitic anhydride followed by glycidyl neodecanoate to achieve good solubility or dispersibility. The grafted oligomers form crystalline domains dispersed in amorphous phase at room temperature. Both pigmented and nonpigmented, high solids, nonaqueous dispersion coatings can be easily formulated from the grafted oligomers with addition of crosslinker such as HMMM or TIC resin. The cured coatings are glossy and have excellent combined hardness and impact resistance. This research provides a simple process for preparing industrially useful, solvent

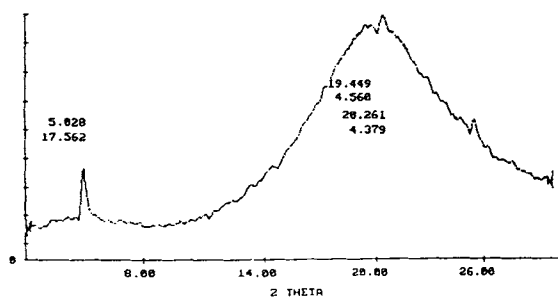


Figure 7 WAXD of 10GTSAGlyd crosslinked with Resimene 746 at room temperature.



Figure 8 Crossed polarizing micrograph of 10GTS-AGlyd crosslinked with Resimene 746 at room temperature.

soluble, or dispersible diols or polyols, and high solids coatings based on them from commodity chemicals.

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Received April 21, 1995

Accepted July 29, 1995