Application Data

MPDiol® Glycol

A Versatile Intermediate for Resin Manufacture

General

2-Methyl-1,3-propanediol (MPDiol® glycol) is a versatile diprimary intermediate for polyester resins manufacture. It is a pumpable liquid at 100% solids. Its nonlinear structure adds value to the end user providing weatherable, extremely flexible liquid resins. This diol can be used in the manufacture of polyester resins and polyester polyol intermediates for use in, for example, OEM, refinish, and coil coatings.

Key Features and Benefits

Liquid Glycol: In typical polyester resin manufacture water is sometimes used to dilute the glycol and pump it into the reactor. This requires unnecessary processing steps. MPDiol is supplied as a pure pumpable, low viscosity liquid and requires no additional solvents for processing addition of diacid in the polyesterification reaction.

Faster Esterification Rates: The diprimary nature of MPDiol ensures better reactivity with diacids. In some cases esterification rates, for the same acid value, are up to 30% faster with MPDiol. Additionally, its boiling point is high allowing for higher processing temperatures without resin yellowing. This processing advantage makes MPDiol glycol an excellent choice in a number of base resins for both saturated and unsaturated polyester resins.

Excellent Storage Stability: The branching of this diol results in resin strands which are unable to align and close pack into crystalline materials. This property increases the shelf-life stability and clarity of the resin before and after formulation.   Additionally, formulators notice lower viscosity and greater organic solubility in these resins as compared to similar, more commonly used resin systems, allowing them to formulate at higher solids content.

Property Benefits

As a monomer, 2-methyl-1,3-propanediol (MPDiol® glycol) contains two primary hydroxyls that quickly react in the presence of diacids during the synthesis of polyester resins. Its higher boiling point allows for higher process temperatures without decomposition or yellowing of the resin.

The methyl group inhibits close packaging between the polyester chains affording less crystallizable resins. (See Figure 1) Finally, since MPDiol is supplied as a pure pumpable liquid, it requires no additional solvents for processing and may eliminate the need for a cook-off step prior to the addition of the diacid(s). Table 1 summarizes the glycol's physical properties

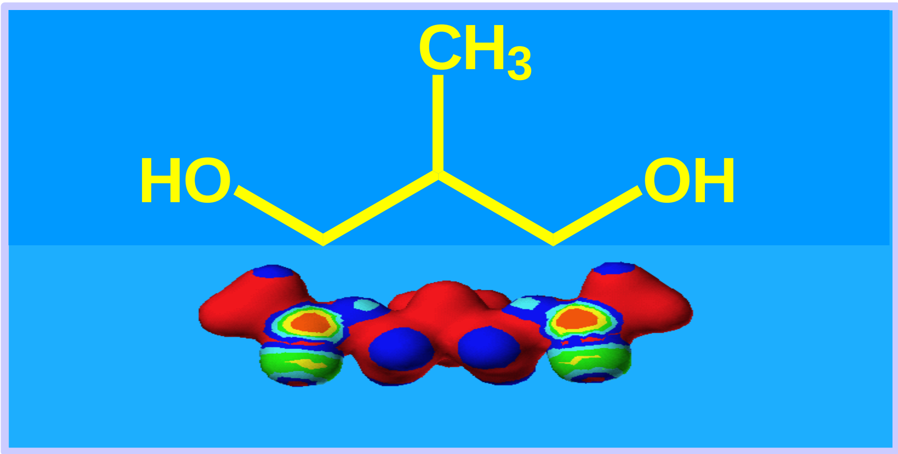

Figure 1. MPDiol 3-D structure

Property	*MPDiol*
Physical State	Liquid
Melting Point	-54°C
Boiling Point	212°C @ 760 mm Hg
Solubility in Water	Infinite
Density	1.01g/cm^3@ 20°C
Flash Point	127°C (closed cup)
Viscosity @ 25°C	165 CST

Table 1 Typical glycol properties

Faster Processing Rates

Typical resin syntheses are performed in batch at 210°C under nitrogen with stirring. The acid number is monitored by titration and continued until the desired acid content is achieved. Several polyester polyols were synthesized to explore the increased reactivity of MPDiol over commonly used diols. Comparative diols were both primary and secondary. The primary diols were used as direct comparisons of processing reactivity. Secondary diols were used for structural and spatial arrangement comparisons. (See Table 2) The composition of each resin is summarized in Table 3.

Diol component	*M. Wt.*	*B. Pt (°C)*	*Melt Pt (°C)*	*Structure*	*Hydroxyls*
MPDiol	90.1	212	-54	Branched	Primary
Ethylene glycol	62.1	196	-13	Linear	Primary
1,3-Propanediol	76.1	214	-27	Linear	Primary
1,4-Butanediol	90.1	230	16	Linear	Primary
1,6-Hexanediol	118	250	43	Linear	Primary
Neopentyl glycol	104	208	125	Branched	Primary
Propylene glycol	76.1	189	<-60	Branched	Prim/Sec
1,3-Butanediol	90.1	203	---	Branched	Prim/Sec
Trimethylpentanediol	146.2	232	52	Branched	Prim/Sec

Table 2 A summary of the Physical and structural properties of commonly used glycols for the design of polyester resins.

Resin Components	*Diprimary Diols moles*	*Primary/Secondary Diols*
Diol	4.30	4.51
Isophthalic Acid	2.00	2.00
Adipic Acid	2.00	2.00
Trimethylolpropane	0.70	0.70

Table 3. Composition of test polyester polyols used for a comparative reactivity study between MPDiol and other diols used in polyester design

Substituting MPDiol, one to one, provided a means for direct comparison and quantification of the structure reactivity correlation between MPDiol and other diols with similar characteristics. The effect of diol selection on the rate of reaction between diacid and glycol and properties of the resulting polymers was measured. All polyester polyols were cooked to the same acid number of approximately 6.5. The differences in the amounts of diol used in the synthesis of diprimary versus primary/secondary polyols stemmed from past experiences in making propylene glycol (PG) based polyesters. Secondary alcohols react slower than primary alcohols. Higher temperatures can solve the reactivity problem but a greater amount of secondary diol is necessary in order to compensate for evaporation. Added excess ensures that the polyols synthesized in this study were of comparable acid numbers. 1,4-Butanediol (1,4-BDO) and trimethylpentanediol (TMPG) yielded lower hydroxyl content polyols because of considerable side reactions. The appearance of broad bands suggestive of a wider range molecular weight distribution is confirmed through gel permeation chromatography (GPC).

The increased amounts of side products show up as tailing in the GPC. This higher molecular weight product contributes to an increase in the final resin viscosity.

The reactivity profile, acid number versus time, of each diol was plotted and compared with MPDiol. (See Figure 2) MPDiol is as reactive as 1,3-propanediol and only slightly less reactive than ethylene glycol. Even the branched nature of MPDiol does not interfere with its reactivity as evidenced by it reacting faster than linear 1,4-BDO and much faster than NPG.

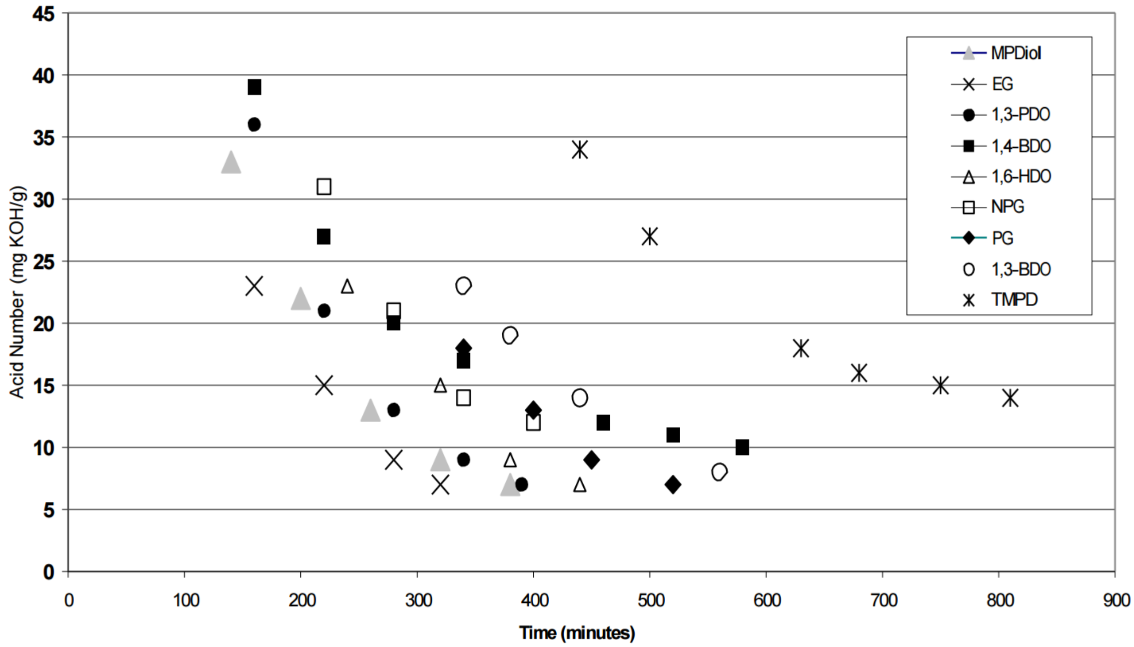

Figure 2. Polyesterification reactivity profile of commonly used glycols as depicted by the decrease in acid number versus time.

Storage Stability

A solvent compatibility test, tendency of the resins to crystallize upon sitting in the solvent, was performed to determine the long-term stability of the various resins. A ninety- percent by weight blend of the polyester polyols to solvent, 1:1 methyl ethyl ketone and propylene glycol methyl ether (ARCOSOLV® PM) was used for the test. Cloudiness, haziness or particulate matter in the resin suggests crystallization. A summary of the results is shown in Table 4. Over a period of three weeks only the MPDiol, 1,6-HDO and the secondary/primary diol based polyesters remained clear. We believe the 1,6-HDO remains clear because of the long chain's tendency to coil. The results also support the belief that branched structures hinder close packing of the chains and in this way inhibit crystallization.

One cannot forget, however, that although secondary glycols provide stable resins these are extremely sluggish under polyesterification conditions. MPDiol has a fast reaction rate as well as maintains a stable clear resin, essentially behaving as a hybrid. This translates to longer shelf life of polyester resin for both the resin manufacturer and formulator. The viscosity of the MPDiol based resins is acceptable and comparable to resins such as 1,6-HDO, PG, 1,3-BDO, and TMPG providing a resin that can be formulated to high solids making it even more attractive.

Diol component	*Gardner-Holt Viscosity*	*Gardner Color*	*Clarity after 3 weeks*
MPDiol	Z-4	1	Clear
Ethylene glycol	Z-5	1	Cloudy
1,3-Propanediol	Z-3	2	Hazy
1,4-Butanediol	Z-6	1	Cloudy
1,6-Hexanediol	Z-1	1	Clear
Neopentyl glycol	Z-6	1	Hazy
Propylene glycol	Z-5	1	Clear
1,3-Butanediol	Z-2	1	Clear
Trimethylpentanediol	Z-4	4	Clear

Table 5 Impact of diol on polyester polyol viscosity at 90% solids in a 1:1 methyl ethyl ketone and propylene glycol methyl ether blend.

Summary

MPDiol presents an alternative monomer for the design of new high performance polyester resins. The diprimary diol possess a higher boiling point than commonly used diols making it easy to increase processing temperature and output without experiencing yellowing due to degradation. The liquid glycol is easily pourable and can be used as 100% solids without the need of a diluent solvent. This eliminates the need for a diluent cook-off step prior to polyesterification decreasing the process cycle time. The resulting transparent polyester resins experience longer shelf life because of molecular branching which prevents close packing and crystallization. The resulting resins are comparable to those available from commonly used diols in resins that are flexible, weatherable, and corrosion resistant. MPDiol can be used as the glycol of choice in a number of base resins for applications in both saturated and unsaturated polyester resins. Additionally, formulations using these resins tend to exhibit lower viscosity when compared to similar, more commonly used resin systems. This means MPDiol based resins, in some cases, can be formulated to higher solids at any given viscosity. This diol can be used in the manufacture of polyester resins and polyester polyol intermediates for use in, for example, OEM, refinish, and coil coatings, as well as in non-coating related applications where polyesters are used. For more information on benefits from using these resins in specific applications please see Application Data Sheets at www.lyondell.com.

Before using a product sold by a company of the LyondellBasell family of companies, users should make their own independent determination that the product is suitable for the intended use and can be used safely and legally.
SELLER MAKES NO WARRANTY; EXPRESS OR IMPLIED (INCLUDING ANY WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE OR ANY WARRANTY) OTHER THAN AS SEPARATELY AGREED TO BY THE PARTIES IN A CONTRACT.

This product(s) may not be used in:
(i) any U.S. FDA Class I, Health Canada Class I, and/or European Union Class I medical devices, without prior notification to Seller for each specific product and application; or
(ii) the manufacture of any of the following, without prior written approval by Seller for each specific product and application: U.S. FDA Class II Medical Devices; Health Canada Class II or Class III Medical Devices; European Union Class II Medical Devices; film, overwrap and/or product packaging that is considered a part or component of one of the aforementioned medical devices; packaging in direct contact with a pharmaceutical active ingredient and/or dosage form that is intended for inhalation, injection, intravenous, nasal, ophthalmic (eye), digestive, or topical (skin) administration; tobacco related products and applications, electronic cigarettes and similar devices, and pressure pipe or fittings that are considered a part or component of a nuclear reactor. Additionally, the product(s) may not be used in: (i) U.S. FDA Class III Medical Devices; Health Canada Class IV Medical Devices; European Class III Medical Devices; (ii) applications involving permanent implantation into the body; (iii) life-sustaining medical applications; and (iv) lead, asbestos or MTBE related applications. All references to U.S. FDA, Health Canada, and European Union regulations include another country's equivalent regulatory classification.

Users should review the applicable Safety Data Sheet before handling the product.

Alkylate, Duopac, Duoprime, Filmex, MPDIOL, Polymeg, SAA-100, SAA-101, TBAc, Tebol, T-Hydro, and Tufflo are trademarks owned or used by the LyondellBasell family of companies.

Duopac, Duoprime, Filmex, MPDIOL, Polymeg, Tebol, T-Hydro and Tufflo are registered in the U.S. Patent and Trademark Office.

Houston, Texas, USA l Tel: +1 713 309 7200 or toll-free within USA +1 888 777 0232
Rotterdam, The Netherlands l Tel: +31 10 275 5500
Hong Kong, China l Tel: +852 2882 2668

© LyondellBasell Industries Holdings, B.V. 2011 www.lyondellbasell.com 2593-V2-0511
Supersedes 2593-V2-0104