

File No: PLC/134

November 1999

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME**

FULL PUBLIC REPORT

Polymer in Desmopan 481

This Assessment has been compiled in accordance with the provisions of the *Industrial Chemicals (Notification and Assessment) Act 1989* (the Act) and Regulations. This legislation is an Act of the Commonwealth of Australia. The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) is administered by the National Occupational Health and Safety Commission which also conducts the occupational health & safety assessment. The assessment of environmental hazard is conducted by the Department of the Environment and the assessment of public health is conducted by the Department of Health and Family Services.

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Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT**Polymer in Desmopan 481****1. APPLICANT**

Bayer Australia Ltd of 875 Pacific Highway, Pymble NSW 2073 has submitted a Polymer of Low Concern notification statement in support of their application for an assessment certificate for Polymer in Desmopan 481. Bayer Australia Ltd has not applied for any information relating to Polymer in Desmopan 481 to be exempt from publication in the Full Public Report and Summary Report.

2. IDENTITY OF THE CHEMICAL**Characterisation as a Synthetic Polymer of Low Concern**

Chemical Name: Hexanedioic acid, polymer with 1,4-butanediol, 1,6-hexanediol, 1,1'-methylenebis(4-isocyanatobenzene) and 2,2'-(1,4-phenylenebis(oxy))bis(ethanol), block

Chemical Abstracts Service (CAS) Registry No.: 122144-14-3

Other Names: Adipic acid, polymer with butylene glycol, hexamethylene glycol, methylene-di-p-phenylene isocyanate and hydroquinone bis (2-hydroxyethyl ether), block

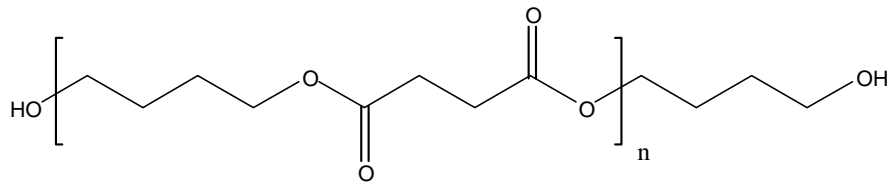
Marketing Name: Polymer in Desmopan 481

Molecular Formula: $[C_{15}H_{10}N_2O_2.C_6H_{14}O_4.C_6H_{14}O_2.C_6H_{10}O_4.C_4H_{10}O_2]_x$

Structural Formula:

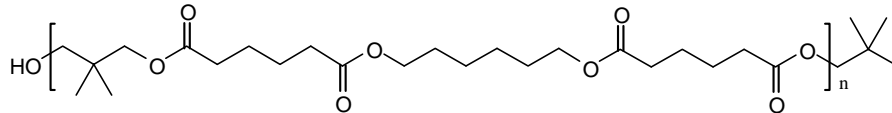
Random block copolymer of different polyadipates, 4, 4'-diphenylmethanedi-isocyanate and 1,4-bis(2-hydroethoxy)benzene.

Poly(butanedioladipate) MW ca 2250



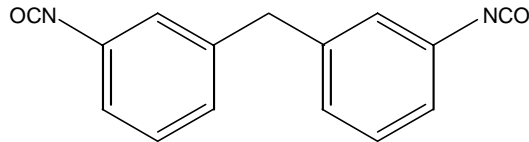
= HOR₁OH

Poly(1,6-hexanediol-2, 2-dimethyl-1,3-propanedioladipate) MW ca 2000



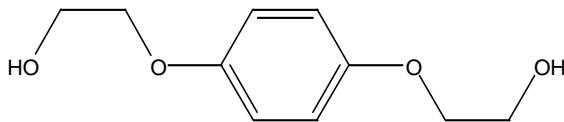
= HOR₂OH

4, 4'-diphenylmethanedi-isocyanate



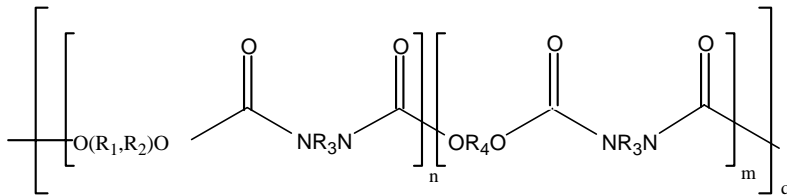
= OCNR₃NCO

1, 4-bis(2-hydroxyethoxy)benzene



=HOR₄OH

Polymer (idealised)



$m=n*1.2$

Number-Average

Molecular Weight (NAMW): Approximately 100,000

Weight-Average

Molecular Weight: Approximately 260,000

Polydispersity: Approximately 2.5

Maximum Percentage of Low Molecular Weight Species <500: 0.67%
<1000: 1.33%

Weight Percentage of Ingredients:

<i>Chemical Name</i>	<i>CAS No.</i>	<i>Weight %</i>
Hexanedioic acid polymer with 2, 2-dimethyl-1, 3-propanediol and 1, 6-hexanediol	25214-14-6	47.58
Hexanedioic acid polymer with 1, 4-butanediol	25103-87-1	21.09
Benzene, 1, 1'-methylenebis[4-isocyanato-	101-68-8	19.50
Ethanol, 2, 2'-[1, 4-phenylenebis(oxy)]bis-	104-38-1	8.28
Hexanedioic acid polymer with 2-ethyl-2-(hydroxymethyl)-1, 3-propanediol and 2, 2'-oxybis(ethanol)	28183-09-7	0.88
1-Butanol, titanium (4+) salt	5593-70-4	0.001

Reactive Functional Groups The polymer is a polyester and does not contain reactive functional groups.

Stability Stable under normal working conditions. Releases isocyanate decomposition products at abnormally high temperatures (>220°C).

Particle Size Not determined

Charge Density No charged groups present

Water Solubility 6mg/L

Method of Detection and Determination: Infra-red spectroscopy; gel permeation chromatography

Comments on Chemical Identity

The polymer meets the criteria for assessment as a synthetic polymer of low concern under Regulation 4A of the *Industrial Chemicals (Notification and Assessment) Act 1989*.

Determination of oligomeric compounds was done by GPC in a tetrahydrofuran (THF) solution. The low molecular weight species above relate to the 60% fraction of THF solubles. This value is corrected by multiplying by 0.60 to give 3.35% for the fraction below 500 Daltons and 4.01% for the fraction below 1000 Daltons. Of these low molecular weight

fractions, 2.68% is likely to be attributable to additives. This is further corrected by subtracting the additive percentage from the above low molecular weight values. The resultant weight percentage of polymer species is therefore 0.67% for the fraction below 500 Daltons and 1.33% for the fraction below 1000 Daltons.

Whilst the notifier has stated that the notified polymer is free of residual monomers, the available GPC slice data indicates a small percentage of low molecular weight species are present. This low molecular weight material is likely to have originated from low molecular weight components in the prepolymers, poly(butanedioladipate) and poly(1, 6-hexanediol-2, 2-dimethyl-1, 3-propanedioladipate).

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20°C and 101.3 kPa:	Yellowish translucent cylindrical granules
Melting Point:	210°C (softening)
Density:	1.21-1.23g/cm ³
Vapour Pressure:	Not determined, but expected to be low
Water Solubility:	Insoluble - see comments below
Partition Co-efficient (n-octanol/water):	Not applicable due to low solubility in water
Hydrolysis as a Function of pH	Not determined – see comments below
Adsorption/Desorption:	Not determined
Dissociation Constant:	Not determined
Flash Point:	Estimated to be >250°C
Flammability Limits:	Not applicable – polymer not flammable
Autoignition Temperature:	Not determined – flash point estimated to be >250°C
Explosive Properties:	Not explosive
Reactivity/Stability:	Stable

Comments on Physico-Chemical Properties

The content of water extractable portions of the notified polymer was determined to be 0.06% (6mg/L) according to EC Regulation L305. The polymer (at 18°C) was ground and sieved.

The 0.125 mm to 0.250 mm fraction was extracted with distilled water for 24 hours using 10g polymer in 1L water. The contents of remaining polymer were determined gravimetrically.

Hydrolysis of the polymer was not tested. Although the ester and urethane linkages of the polymer have the potential to hydrolyse, it is anticipated that the low solubility of the polymer will prevent hydrolysis under environmental conditions.

4. PURITY OF THE CHEMICAL

Degree of Purity: >97%

Maximum Content of Residual Monomers: <1%

Impurities none

Additives/Adjuvants: <3%

Chemical name: Octadecanamide, N,N'-1, 2-ethanediylbis

CAS No.: 110-30-5

Weight percentage: 1.05

Comment: Not listed as a hazardous substance (National Occupational Health and Safety Commission, 1999).

Chemical name: Benzeneamine, N,N'-methanetetraylbis[2, 6-bis-(1-methylethyl)-

CAS No.: 2162-74-5

Weight percentage: 0.54

Comment: Not listed as a hazardous substance (National Occupational Health and Safety Commission, 1999).

Chemical name: Paraffin oils

CAS No.: 8012-95-1

Weight percentage: 0.4

Comment: Listed as a hazardous substance (National Occupational Health and Safety Commission, 1999). No risk phrases have been assigned.

Chemical name: Siloxanes and Silicones, di-methyl

CAS No.: 63148-62-9

<i>Weight percentage:</i>	0.36
<i>Comment:</i>	Not listed as a hazardous substance (National Occupational Health and Safety Commission, 1999).
<i>Chemical name:</i>	Siloxanes and Silicones, di-methyl, di-phenyl
<i>CAS No.:</i>	68083-14-7
<i>Weight percentage:</i>	0.26
<i>Comment:</i>	Not listed as a hazardous substance (National Occupational Health and Safety Commission, 1999).
<i>Chemical name:</i>	Benzenepropanoic acid, 3, 5-bis(1, 1-dimethylethyl)-4-hydroxy-, 2, 2-bis[[3-[3, 5-bis(1, 1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxyl]methyl]-1, 3-propanediyl ester
<i>CAS No.:</i>	6683-19-8
<i>Weight percentage:</i>	0.07
<i>Comment:</i>	Not listed as a hazardous substance (National Occupational Health and Safety Commission, 1999).

5. USE, VOLUME AND FORMULATION

The notified polymer will be fully imported into Australia in Desmopan 481 at a rate of 10 tonnes per annum for the first 2 years and 30 tonnes per annum for years 3 to 5. The percentage of notified polymer in imported Desmopan 481 is > 95%. No reformulation will take place.

The notified polymer will be imported as soft cylindrical granules in 130-140 kg drums and transported directly to a single site for end use. The polymer is a component of thermoplastic urethane used in injection moulding (processing temperatures 165-220°C) where finished articles are produced and no further processing is required.

6. OCCUPATIONAL EXPOSURE

The notified polymer is transported to the customer's store in 130-140 kg drums. No occupational exposure is expected during transport and storage unless the packaging is damaged.

The drums of polymer are then moved to the injection moulding machines via forklift. They are then unsealed and a vacuum hose is used by the plant operator to transfer the product into the machine. The injection moulding machine is fully automatic and enclosed with finished articles ejected in 3-10 minutes. The amount of Desmopan 481 used per day depends on the batch size, and could be 500-5000kg/day. The finished parts are removed, packed and

distributed to customers. The entire operation is conducted in a fully ventilated environment. One (1) worker is involved with the process at each injection moulding machine (6 days of 8 hours each) and two (2) workers are involved in packing and transport.

According to the notifier, the injection moulding process using the notified polymer is routinely conducted at temperatures 165-220°C. At these normal operating conditions, small amounts of isocyanates are released. The notifier has provided study data showing that at temperatures of 190-210°C, <0.0001mg isocyanates/m³ air are produced. At higher working temperatures resulting from incorrect plant operations, significantly larger amounts of isocyanate decomposition products are liberated. Data supplied by the notifier show that at 230°C, 0.002-0.007mg/m³ are released.

Spills of polymer and rejected articles that are first reground into granules, are reused. There is the possibility of occupational exposure to polymer dust generated in the vicinity of the grinding machinery from this procedure.

7. PUBLIC EXPOSURE

It is expected that during transport, storage and use, exposure of the general public to the notified chemical will be very low.

8. ENVIRONMENTAL EXPOSURE

Release

Release of the notified polymer to the environment during article manufacture is expected to be minimal. The polymer will be vacuum transferred to a hopper, heated and fed through extrusion and moulding machinery. Clean waste products will be reground and reused. Contaminated polymer waste will be deposited to landfill - estimated to account for approximately 0.5% of the annual import volume.

Residues in drums are unlikely to remain due to the large granular nature of the commercial product. Drums will be reused at the site or sent to landfill. There is potential for accidental release during transport but this risk is considered to be low because spills will be easily contained and cleaned up.

Fragments of the notified polymer may also be released as a result of wear and tear on the moulded end-product article. This form of release is expected to be site limited and comparatively minor, relative to the amount of waste generated by disposal of the article at the end of its useful life.

The majority of the notified polymer is not expected to be released to the environment until the article is discarded to landfill at the end of its useful life. The notifier did not indicate the expected lifespan of the moulded articles. However, it is assumed that close to 100% of the notified polymer will ultimately be disposed of to landfill despite being suitable, after appropriate treatment, for mechanical recycling.

Fate

During normal batch processing, small amounts of isocyanates ($< 0.0001 \text{ mg/m}^3$) are produced. These are mainly as di-isopropyl-phenylisocyanate and diphenylmethane-4, 4-di-isocyanate. At temperatures greater than 220°C , considered abnormally high for processing conditions, the notified polymer is likely to decompose producing higher quantities of isocyanate (0.002 to 0.007 mg/m^3).

The ester and urethane linkages of the polymer have the potential to hydrolyse. However, it is anticipated that the low solubility of the polymer will prevent hydrolysis under environmental conditions.

Degradation information was not provided by the notifier but it is expected that the polymer will not readily degrade once disposed of to landfill. Bioconcentration and leaching are considered to be unlikely, due to the high molecular weight of the polymer and its low solubility.

9. EVALUATION OF TOXICOLOGICAL DATA

No toxicology data were submitted.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

No ecotoxicological data were submitted.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

It is anticipated that close to 100% of the notified polymer will eventually be released to the environment. Faulty moulded objects or spilled polymer will be returned to the moulding machinery and waste during the manufacturing process is expected to be minimal.

Moulded articles will be disposed of to landfill at the end of their useful life. Disposal of the notified polymer to landfill, either in pellet form or as finished article, is unlikely to present a hazard to the environment. The notified polymer is insoluble and therefore is expected to be immobile within landfill sites.

Bioconcentration and leaching of the polymer are considered to be unlikely, due to the high molecular weight of the polymer and insolubility. Although no polymer degradation information was provided, it is expected that the polymer and moulded products will degrade very slowly via biotic and abiotic processes.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

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No toxicological data on the notified polymer have been submitted. Given the negligible residual monomer content of the notified polymer and high molecular weight (NAMW 100,000), it is not expected to traverse biological membranes. According to the notifier, under normal conditions of use, the polymer will not hydrolyse, undergo significant photo- or thermal degradation and will not depolymerise.

All but one of the polymer additives are not listed as hazardous (National Occupational Health and Safety Commission, 1999). The additive paraffin oils are listed as hazardous (National Occupational Health and Safety Commission, 1999) but no risk phrases have been assigned.

Occupational Health and Safety

Under normal use conditions, exposure to the notified polymer is low due to its physical form (granules) and enclosed nature of the injection moulding process. Considering the low hazard of the polymer, the risk of adverse health effects is very low during routine operations. However, toxicological information on the Material Safety Data Sheet (MSDS) for the product indicates that minute quantities of isocyanates may be released into the air during normal processing (0.0001 mg/m^3 , $< 210^\circ\text{C}$). If recommended working temperatures are exceeded for any reason, these levels would increase significantly and may cause respiratory irritation and/or sensitisation in exposed workers. Under normal conditions of use, isocyanate levels should not exceed the Australian exposure standards of 0.02 mg/m^3 TWA, 0.07 mg/m^3 STEL (National Occupational Health and Safety Commission, 1995). Exposure monitoring will be needed.

During recycling of the polymer, the grinding process by which faulty manufactured parts are reduced to polymer granules suitable for remoulding may produce polymer dust. The levels of dust expected during recycling have not been quantified. The MSDS for the notified polymer recommends that operators wear respirators during this grinding process and includes the NOHSC exposure standard for inspirable dust (10 mg/m^3). Given the possibility of workers being exposed to small amounts of the notified polymer and decomposition products by inhalation, it is important adequate ventilation be provided in the workplace. Any reprocessing of polymer articles will need to be under conditions that control the release of isocyanate decomposition products. The MSDS directs users to contact the manufacturer for more information on this.

Due to the expected low exposure during transport and storage, the health risk is negligible during these operations, unless accidental spillage occurs.

Public Health

The notified polymer is intended for industrial use as a thermoplastic polyurethane solid and public exposure would only occur in the event of an accidental spill, fire or after disposal. Consequently, the potential for public exposure to the notified polymer during all phases of its life cycle is considered to be very low.

Based on the above information, it is considered that Polymer in Desmopan 481 will not pose a significant hazard to public health when used in the proposed manner.

13. RECOMMENDATIONS

1. To minimise occupational exposure to Polymer in Desmopan 481 the following guidelines and precautions should be observed:
 - Ensure that personal protective equipment worn conforms to the relevant Australian standard: Safety goggles - Australian Standard (AS) 1336 (Standards Australia, 1994) and Australian/New Zealand Standard (AS/NZS) 1337 (Standards Australia/Standards New Zealand, 1992); Industrial clothing - AS 2919 (Standards Australia, 1987) and AS 3765.2 (Standards Australia, 1990); Impermeable gloves or mittens - AS 2161 (Standards Australia/Standards New Zealand, 1998); Occupational footwear - AS/NZS 2210 (Standards Australia/Standards New Zealand, 1994).
 - Spillage of the notified chemical should be avoided. Spillages should be swept up promptly and put into containers for disposal;
 - Good personal hygiene should be practised to minimise the potential for ingestion;
 - A copy of the MSDS should be easily accessible to employees.
2. The employer should ensure that isocyanate levels are maintained below exposure standards (National Occupational Health and Safety Commission, 1995) in the injection moulding area and other remelting/reprocessing areas.
3. If the conditions of use are varied, greater exposure of the public may occur. In such circumstances, further information may be required to assess hazards to public health.

14. MATERIAL SAFETY DATA SHEET

The MSDS for the notified chemical was provided in accordance with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (National Occupational Health and Safety Commission, 1994).

This MSDS was provided by the applicant as part of the notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of the applicant.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under subsection 64(1) of the Act, secondary notification will be required if the polymer characteristics cease to satisfy the criteria under which it has been accepted as a Synthetic Polymer of Low Concern. Secondary notification of the notified polymer shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

16. REFERENCES

National Occupational Health and Safety Commission (1994) National Code of Practice for the Preparation of Material Safety Data Sheets [NOHSC:2011(1994)]. Australian Government Publishing Service, Canberra.

National Occupational Health and Safety Commission (1995) Adopted National Exposure Standards for Atmospheric Contaminants in the Occupational Environment, [NOHSC:1003(1995)]. In: ed. Exposure Standards for Atmospheric Contaminants in the Occupational Environment: Guidance Note and National Exposure Standards. Australian Government Publishing Service, Canberra, .

National Occupational Health and Safety Commission (1999) List of Designated Hazardous Substances [NOHSC:10005(1999)]. Australian Government Publishing Service, Canberra.

Standards Australia (1987) Australian Standard 2919-1987, Industrial Clothing. Standards Association of Australia, Sydney.

Standards Australia (1990) Australian Standard 3765.2-1990, Clothing for Protection against Hazardous Chemicals Part 2 Limited protection against specific chemicals. Standards Association of Australia, Sydney.

Standards Australia (1994) Australian Standard 1336-1994, Eye protection in the Industrial Environment. Standards Association of Australia, Sydney.

Standards Australia/Standards New Zealand (1992) Australian/New Zealand Standard 1337-1992, Eye Protectors for Industrial Applications. Standards Association of Australia/Standards Association of New Zealand, Sydney/Wellington.

Standards Australia/Standards New Zealand (1994) Australian/New Zealand Standard 2210-1994, Occupational Protective Footwear. Standards Association of Australia/Standards Association of New Zealand, Sydney/Wellington.

Standards Australia/Standards New Zealand (1998) Australian/New Zealand Standard 2161.2-1998, Occupational protective gloves, Part 2: General requirements. Standards Association of Australia, Sydney.