The pure compound does not polymerize at room temperature and can be preserved without an inhibitor. 2,4-Diallyloxy-6-phenoxy-1,3,5-triazine at room temperature polymerizes very slowly in the presence of 0.1–0.5% dibenzoyl peroxide. An increase in temperature to 60°–80°C in the presence of 0.1% dibenzoyl peroxide causes a rapid polymerization of the compound, the first symptom of which can be observed after 90 min, and the hard polymer is ready after 270 min.

Without an initiator the polymerization starts after 60 min at 150°C and the reaction is rapid at the boiling point.

The polymerized 2,4-diallyloxy-6-phenoxy-1,3,5-triazine is a solid transparent light yellow compound and its physical, mechanical and thermal properties are given in *Table 2*.

Particular kinetic investigations of the homo- and copolymerization reactions, with chosen vinyl monomers, are presently being carried out. Their results will be published in a future paper.

Table 2 Physical, mechanical and thermal properties of poly(2,4-dialkyloxy-6-phenoxy-1,3,5-triazine)

Density (kg m^{-3})	1490
Tensile strength (Nm^{-2})	$391\cdot10^5$
Bending strength (Nm^{-2})	$108\cdot10^5$
Dynstat impact strength (Nmm^{-2})	$147\cdot10^2$
Brinell hardness	17.5
Vicat softening point (°C)	110
Temperature bending point under loading (°C)	91
Temperature half decomposition in air (°C)	318
Temperature half decomposition in nitrogen (°C)	340
Temperature decarbonization (°C)	380

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Activated derivatives of succinic and glutaric half-esters of polypropylene glycols, and their exchange reactions with hydroxy- and amino-compounds

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Succinic and glutaric halfesters of polypropyleneglycols have been prepared, and transformed into the corresponding imidazolides and benzotriazolides. The exchange reactions of the latter with hydroxylated and aminated compounds have been studied.

Keywords Functionalized oligomers; carboxylated polypropylene glycols; imidazolides; benzotriazolides; exchange reactions

INTRODUCTION

In previous papers we have described the ability of several polymeric and oligomeric activated esters and amides to react selectively with hydroxylated or aminated compounds, giving polymeric and oligomeric esters or amides which are not easily obtained by other means[1–4].

Other derivatives of similar activity were also prepared independently by Ringsdorf and his colleagues[5], and by Winston and Mazza[6]. The main purpose of these studies was to develop new synthetic routes to oligomeric or polymeric derivatives of pharmocologically active compounds.

Following this line, we thought it might be interesting to report on the synthesis of succinic and glutaric half-esters of polypropylene glycols, and of the corresponding imidazolides and benzotriazolides. The exchange reactions of the latter with model hydroxylated and aminated compounds were also studied.

Succinic and glutaric half-esters of polypropylene glycols

Polypropylene glycol samples (purchased from Fluka A.G., Buchs S.G., Switzerland) having $\bar{M}_n$ 425 (I) and 725 (II) were chosen as starting materials. Their succinic (III,

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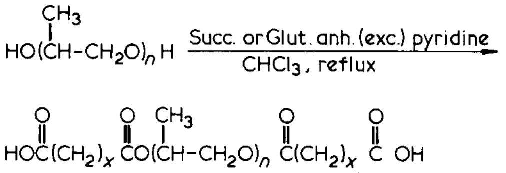
V) and glutaric (IV, VI) half-esters were prepared by reacting I and II with succinic or glutaric anhydride in chloroform solution in the presence of pyridine:



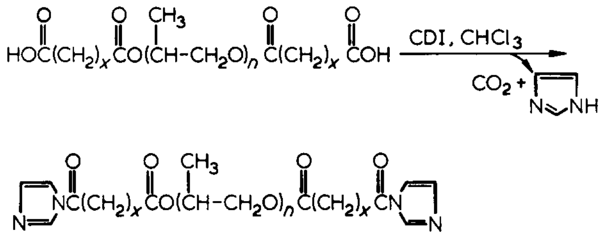
$$HO(\overset{CH_3}{\overset{|}{C}}H-CH_2O)_nH \xrightarrow[CHCl_3,\ reflux]{Succ.\ or\ Glut.\ anh.\ (exc.)\ pyridine} HO\overset{O}{\overset{\|}{C}}(CH_2)_x\overset{O}{\overset{\|}{C}}O(\overset{CH_3}{\overset{|}{C}}H-CH_2O)_n\overset{O}{\overset{\|}{C}}(CH_2)_x\overset{O}{\overset{\|}{C}}OH$$

I: $\bar{n}=7$; III: $\bar{n}=7$, $x=2$; IV: $\bar{n}=7$, $x=3$;
II: $\bar{n}=12.2$; V: $\bar{n}=12.2, x=2$; VI: $\bar{n}=12.2, x=3$.

The products, after isolation (see Experimental section) were characterized by elemental analysis, and titration. The degree of esterification was, in all cases, practically complete. These half-esters were easily extracted from their ether and chloroform solutions by water at a pH above 7, but at acidic pH the reverse was true: this was of advantage during their isolation from the reaction mixtures. All of them are viscous liquids, soluble in alcohols, ethers, chlorinated solvents, dimethylsulphoxide (DMSO), dimethylformamide (DMF), and aromatic hydrocarbons, but practically insoluble in water and aliphatic hydrocarbons. They are less hydrophilic and more lipophilic than other polyoxylalkylenglycols half-esters previously prepared by our group[1]. This may be of advantage in their pharmacological applications.

Imidazolides of succinic and glutaric half-esters of polypropyleneglycols, and their exchange reactions

The imidazolides of III, IV, V and VI were prepared by allowing them to react with *N*,*N'*-carbonyldiimidazole (CDI) in chloroform solution:



VII: $\bar{n}=7$, $x=2$; VIII: $\bar{n}=7$, $x=3$;
IX: $\bar{n}=12.2, x=2$; X: $\bar{n}=12.2, x=3$.

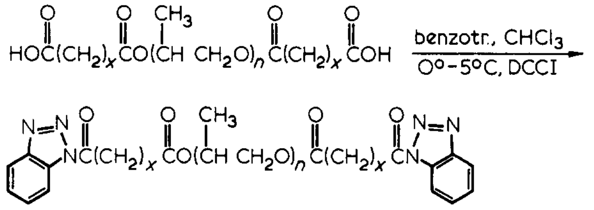
These compounds are very sensitive to atmospheric moisture. Usually they were not isolated, and in the exchange reactions their solutions were used as obtained.

The ability of compounds VII–X to enter into exchange reactions with amines was tested with morpholine: by allowing them to react with a two-fold excess of morpholine for about 16 h at room temperature, a practically quantitative exchange was obtained.

The ability of compounds VII–X to enter into exchange reactions with hydroxylated compounds was tested with β-phenylethanol, 4-chlorophenol and α-phenylethanol. The exchange reactions were always run at 55°C for 16–24 h. The characterization of the exchange products by elemental analysis and n.m.r. spectroscopy showed that in the first two cases a nearly quantitative degree of esterification was reached, while with the secondary alcohol a degree of esterification near 70% was obtained in all cases.

Benzotriazolides of succinic and glutaric half-esters of polypropylene glycols, and their exchange reactions

The benzotriazolides of compounds III, IV, V and VI were prepared by condensation with benzotriazole in the presence of dicyclohexylcarbodiimide (DCCI), in anhydrous, alcohol-free chloroform:



XI: $\bar{n}=7$, $x=2$; XII: $\bar{n}=7$, $x=3$;
XIII: $\bar{n}=12.2, x=2$; XIV: $\bar{n}=12.2, x=3$.

The purification of compounds XI–XIV from dicyclohexylurea (DCU) and from the excess of benzotriazole was difficult and so few perfectly pure products were obtained (see the Experimental section). In all cases, they are viscous liquids with the same solubility characteristics of the starting half-esters.

The reactivity of these benzotriazolides towards aminated compounds was tested with morpholine, under the same conditions used for the imidazolides.

The results were similar to those obtained with imidazolides. As the reactivity of polymeric and oligomeric benzotriazolides is known to be considerably lower towards hydroxylated compounds[1–3], we thought it interesting to examine the progress, with time, of the exchange reaction with a secondary alcohol, α-phenylethanol. Three sets of experiments were performed. In type A experiments, compounds XI–XIV were allowed to react with a 20% excess α-phenylethanol in chloroform solution at 55°C and, according to previous findings[1–3], in the absence of catalysts the exchange reaction was very slow. For instance, the elemental analysis of the product obtained from compound XIII, after a reaction time of 72 h, indicated a degree of esterification of about 37%. In type B experiments, triethylamine (4 moles/mole benzotriazolide) was added to the reacting mixture, all other conditions being equal. In agreement with previous results obtained with other polymeric or oligomeric benzotriazolides[1–3], the reaction rates were found to be considerably increased with respect to type A experiments. For instance, the elemental analysis of the products obtained by sampling the reacting solution of compound XIII with α-phenylethanol after 8, 48 and 72 h, showed degrees of esterification of about 66%, 89% and 93%, respectively.

Since *N*,*N*-dimethyl-4-pyridinamine (DMPA) is known to be a very effective acylation catalyst[7], its efficiency was tested with compounds XI–XIV in type C experiments, by adding DMPA (2.2 moles/mole benzotriazolide) to the reacting mixture, all other conditions being the same. The reaction rates were actually still found to be enhanced with respect to type B experiments. For example, the elemental analyses of the exchange products obtained by sampling the reacting solution after 2, 8, 48 and 72 h indicated decrees of esterification of about 73%, 80% and 94%, respectively.

EXPERIMENTAL

N.m.r. spectra ($CDCl_3$, TMS) were recorded on a Varian 60 MHz spectrometer. Found and calculated ratios between integrated signals pertinent to the total hydrogens of polypropyleneglycol half-ester moiety ($=\int$PPG), and benzotriazole or substituted phenyl hydrogens ($=\int$Ar), are reported.

Succinic and glutaric half-esters of polypropyleneglycols (III–VI)

Polypropyleneglycols 425 (I) and 725 (II) were dried over anhydrous $CaSO_4$ before reaction.

In a typical procedure, 10 g (13.8 mmol) of compound II were dissolved in dry (CaH_2), alcohol free chloroform (100 ml), and succinic anhydride (6.9 g, 69 mmol) and dry pyridine (5.6 ml, 69 mmol) were added. The reaction mixture was refluxed for 24 h, then it was evaporated to dryness *in vacuo*, and the residue was dissolved in ether (200 ml). After eliminating most of the unreacted anhydride by filtration, the ethereal solution was extracted with 10% aq. $NaHCO_3$ (3 × 50 ml); the combined aqueous extracts were cooled to 0°–5°C, acidified with HCl and extracted with $CHCl_3$ (3 × 50 ml). The combined organic layers were then washed with water (4 × 30 ml), dried (anhydrous Na_2SO_4), filtered, evaporated to dryness *in vacuo*, and extracted with n-heptane before drying to constant weight at room temperature and 0.1 mm. Yield 11.5 g (90%).

Analysis: found: C 58.02; H 8.85
calculated: C 57.80; H 9.05.

Titration (in MeOH solution, with methanolic 0.1N KOH and phenolphthalein):

found: 2.18 meq/g*
calculated: 2.16 meq/g.

Compounds III, IV and VI were prepared in the same way, starting from the corresponding quantities of compounds I or II, pyridine and succinic or glutaric anhydride. Yields were in all cases about 90%.

Analyses: (III) found: C 55.14; H 8.12
calculated: C 55.73; H 8.39
(IV) found: C 57.43; H 9.11
calculated: C 57.04; H 8.65
(VI) found: C 58.40; H 9.08
calculated: C 58.62; H 9.21.

Titrations: (III) found: 3.18 meq/g*
calculated: 3.2 meq/g
(IV) found: 2.99 meq/g
calculated: 3.06 meq/g
(VI) found: 1.98 meq/g
calculated: 2.1 meq/g

Imidazolides of compounds III–VI (VIII–X) and their exchange reactions

In a typical procedure, V (2 g, 2.16 mmol) was dissolved in dry $CHCl_3$ (20 ml), CDI (840 mg, 5.2 mmol) was added and the mixture was allowed to react at room temperature under stirring until effervescence ceased (~30 min).

For the amidation reaction, morpholine (0.75 ml, 8.6 mmol) was added; the reaction mixture was left at room temperature for 16 h, the extracted with 1% aqueous CH_3COOH (2 × 15 ml) and water (3 × 15 ml). The organic layer was dried (anhydrous Na_2SO_4), evaporated to dryness *in vacuo* and the residue finally washed with n-heptane before drying to constant weight. Yield: 2.2 g (95%).

Analysis: found: C 59.19; H 9.47; N 2.31
calculated: C 59.32; H 9.20; N 2.63

For the esterification reactions, (1) β-phenylethanol (0.8 ml, 6.5 mmol), or (2) α-phenylethanol (0.8 ml, 6.5 mmol), or (3) 4-chlorophenol (830 mg, 6.5 mmol) was added and the reaction mixture was kept at 55°C for 16–24 h. In the first two cases, the reaction mixtures were then treated as described in the case of morpholine, by substituting ~0.2 N aqueous HCl for CH_3COOH. During the isolation of the exchange product with α-phenylethanol, any imidazolide groups which might have survived at the end of the reaction was purposely hydrolysed. In the third case, the reaction mixture was evaporated to dryness *in vacuo*, the residue dissolved in ether (50 ml) and the ethereal solution washed with ~0.2 N aqueous HCl (2 × 15 ml), water (2 × 15 ml), ~0.2 N aqueous NaOH (2 × 15 ml) and water (3 × 15 ml). After drying over anhydrous Na_2SO_4 and filtering, it was finally evaporated to dryness *in vacuo* and dried to constant weight. Yields ranged between 70 and 90%.

Analyses: (1) found: C 63.91; H 8.78. calculated for 100% esterification: C 64.13; H 8.81
(2) found: C 62.49; H 9.00. calculated for 75% esterification: C 62.55; H 8.87
(3) found: C 59.36; H 7.84. calculated for 100% esterification: C 59.22; H 7.83

Nitrogen was found to be absent in the exchange products by qualitative tests (Lassaigne):

N.m.r.: (1) found: $$\frac{\int PPG}{\int Ar} = 8.36$$

calculated: $$\frac{\int PPG}{\int Ar} = 8.10$$

2) found: $$\frac{\int PPG}{\int Ar} = 10.56$$

calculated for 75% esterification: $$\frac{\int PPG}{\int Ar} = 10.8$$

(3) found: $$\frac{\int PPG}{\int Ar} = 10.40$$

calculated: $$\frac{\int PPG}{\int Ar} = 10.13$$

Compounds VII, VIII and X were prepared as described for compound IX, and their exchange reactions were performed analogously, giving similar results.

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* meq/g here means: mmol COOH-groups/g

Benzotriazolides of compounds III–VI (XI–XIV)

In a typical procedure, V (8.7 g, 9.4 mmol) was dissolved in dry $CHCl_3$ (90 ml) and the solution was cooled to 0°–5°C. Benzotriazole (2.7 g, 22.7 mmol) and DCCI (4.7 g, 22.7 mmol) were added; the reaction mixture was left under stirring for 2 h at 0°–5°C and finally for 12 h while rising to the room temperature. It was then filtered and evaporated to dryness *in vacuo*; the residue was dissolved in dry ether (20 ml), the solution filtered and evaporated again to dryness. This treatment was repeated several times until no precipitate of dicyclohexylurea could be detected during dissolution. The product was finally extracted with dry n-heptane and dried at room temperature and 0.1 mm. Yield: 10 g (95%).

Analysis: found: C 58.72;
H 7.90; N 7.92
calculated: C 60.20;
H 7.96; N 7.45

N.m.r.: found: $\frac{\int PPG}{\int Ar} = 9.82$

calculated: $\frac{\int PPG}{\int Ar} = 10.13$

Compounds XI, XII and XIV were prepared in the same way, using the corresponding quantities of compounds III, IV or VI, benzotriazole and DCCI; in all cases the n.m.r. spectra and elemental analyses were consistent with the proposed structures.

Exchange reactions of compounds XI–XIV with morpholine

In a typical procedure, XIII (700 mg, 0.62 mmol) was dissolved in dry $CHCl_3$ (7 ml) and morpholine (0.22 ml, 2.48 mmol) was added. The reaction mixture was left at room temperature for 16 h, then treated as described in the case of the analogous exchange reaction of the corresponding imidazolide. Yield: 590 mg (~90%).

Analysis: found: C 60.32;
H 9.60; N 3.48
calculated: C 59.32;
H 9.20; N 2.63

The infra-red spectrum (film) of the amidation product showed the complete disappearance of the characteristic triplet centred at about 770 cm^{-1} which may be attributed to substituted benzotriazole. The presence of a small impurity of dicyclohexylurea could be detected by t.l.c. (SiO_2, Et_2O). In fact, the benzotriazolide used in this reaction had not been especially purified.

Exchange reactions of compounds XI–XIV with α-phenylethanol

Type A experiments. 1 g (0.89 mmol) XIII was dissolved in dry $CHCl_3$ (10 ml) and α-phenylethanol (0.26 ml, 2.2 mmol) was added. The reaction mixture was kept at 55°C for 72 h, then it was evaporated to dryness *in vacuo*. The residue was dissolved in dry ether, the solution filtered and evaporated again to dryness. The product was then dissolved once more in ether, and the ethereal solution was washed with ~0.2 N aqueous HCl (2 × 10 ml) and water (3 × 10 ml). The starting benzotriazolide had previously been found to be unaffected by this treatment. The ethereal solution of the exchange product was finally dried over anhydrous Na_2SO_4; filtered and evaporated, and the residue dried to constant weight.

Table 1 Type B and C experimental results for nitrogen analyses and degree of esterification

Experiment	Reaction time (h)	Found (N%)	Corresponding esterification (%)
B	8	2.52	66
	48	0.79	89
	72	0.57	92
C	2	2.06	72
	8	1.42	80
	48 and 72	0.49	93

Analysis: found: C 61.27;
H 8.61; N 4.30
calculated for 37% esterification: C 61.66;
H 8.27; N 4.69

Type B and type C experiments. These experiments were performed according to the same procedure as for type A, apart for the addition of triethylamine or DMPA, respectively (see the text). The nitrogen analyses of the products are given in *Table 1*. Carbon and hydrogen analyses, whenever tried, confirmed the results in *Table 1*. For instance, analyses of a type B product after 72 h (1), and a type C product after 8 h (2), gave the following results:

(1) C 63.59, H 8.74 (calculated for 92% exterification: C 63.82, H 8.74); (2) C 62.91, H 8.66 (calculated for 80% esterification: C 63.34, H 8.64).

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