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POLYMERIZATION IN LIQUID CRYSTAL — XVIII*

EFFECT OF THE POLYETHYLENEOXIDE MAIN CHAIN ON THE PROPERTIES OF POLYMERS CONTAINING MESOGENIC GROUPS IN THE SIDE CHAIN

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Abstract—The effect of the main chain on the mesomorphic properties was studied on the basis of the three-component thermodynamic model of polymers containing mesogenic groups in the side chain. Poly(ethylene oxide) oligomers substituted with mesogenic groups were prepared by reacting epichlorohydrin with mesogenic molecules. It was established that the glass transition temperatures of these oligomeric products were markedly reduced in comparison to polyacrylates containing the same rigid core. The relatively flexible main chain increases the clearing point relative to that of the monomer. Clearing point rises with length of the main chain. A flexible main chain suppresses the vibration of the rigid cores thus increasing the thermal stability of the mesomorphic structure. No explanation was found for the exothermic latent heat of 170 J/g observed during the first melting of the cholesteryl succinyl epoxypropionate oligomers and polymers.

INTRODUCTION

It has been demonstrated [1,2] that properties of mesomorphic materials can be deduced from the presence of two kinds of molecular environment in the system having very different inherent transition temperatures, *viz*. a rigid core and a rather flexible mobile matrix. In mesomorphic polymers containing the mesogenic group (rigid core) in the side chain, the flexible matrix is divided into two interacting molecular regions, *viz*. the main chain and the flexible chain segments connected directly to the rigid core. To study the effects of side chains on the properties of mesomorphic polymers, the role of the spacer (the interconnecting section between the main chain and the core) was mainly considered [3–7]; the effect of the main chain on the properties of the mesomorphic polymers has been studied only for polysiloxane main chains (Finkelmann and Ringsdorf) [7].

Polymers thoroughly investigated include essentially three kinds of main chain. Polymethacrylate main chains are considered rigid [2–6] and polysiloxane main chains flexible [7] while chains of intermediate flexibility are polyacrylates [2–6]. There are some other intermediate cases in mesomorphic polymers (such as polyvinylethers and polyvinylesters) but they have not been investigated systematically [8–10].

Previous comparisons showed that the glass transition temperature of mesomorphic polymers rises with increasing rigidity of the polymeric main chain, narrowing the temperature range of the mobile mesomorphic state.

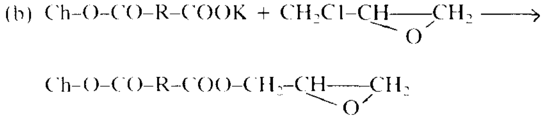
In the present paper, effects of the polymer main chains in polyethers (rather flexible but more stable than the polysiloxanes) are studied. The previously described [1] three-component model of mesomorphic polymers was applied.

It is known [11] that rigidity of polymers having a polymethylene main chain is enhanced by the repulsion potential of the side chains on the main chain. By increasing the distances between the side chains along the main chain (e.g. by insertion of methylene groups), the influence of the side chains on the enhancement in rigidity is diminshed. It seemed reasonable therefore to select the poly(ethylene oxide) main chain for investigation since the ethereal oxygens made the main chain itself rather flexible; the energy barrier for conformational isomerization is extremely low. On the other hand, the substituents are located on every third atom along the main chain allowing the incorporation of quite bulky rigid cores (such as cholesteric structures) without any repulsion even in the *all-trans* configuration, in coplanar parallel situation. It was supposed that, in this case, incorporating even a short spacer group would give a good chance for the mesomorphic (smectic, nematic or cholesteric) to be a mobile mesomorphic phase.

EXPERIMENTAL

Preparations of monomers were carried out by the following reactions:

(a) $\text{Ch–O–CO–R–COOH} \xrightarrow[\text{CHCl}_3]{\text{KOH}} \text{CH–O–CO–R–COOK}$



(b) $\text{Ch–O–CO–R–COOK} + \text{CH}_2\text{Cl–}\underset{\diagdown\,\text{O}\,\diagup}{\text{CH——CH}_2} \xrightarrow{\text{Cat.}}$

$\text{Ch–O–CO–R–COO–CH}_2\text{–}\underset{\diagdown\,\text{O}\,\diagup}{\text{CH——CH}_2}$

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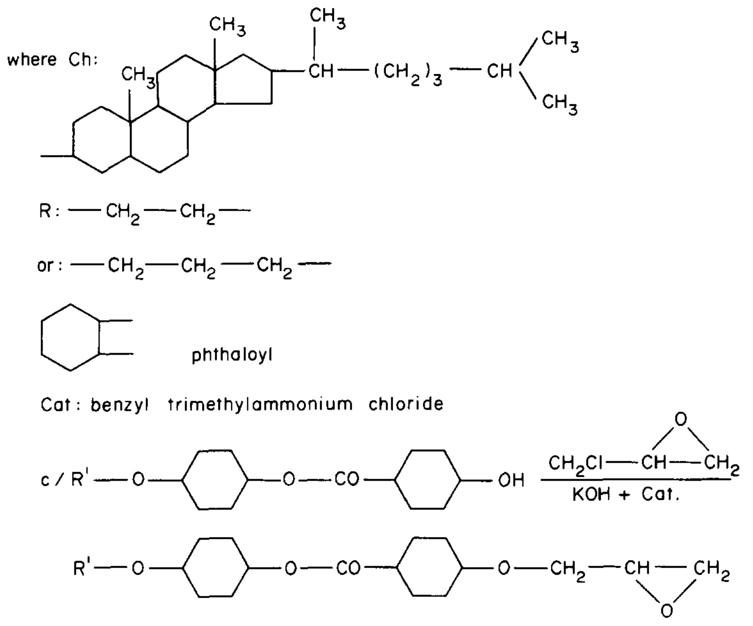
* Part XVII: cf. Ref. 2.



where R': $-CH_3$ or $-C_4H_9$.

Preparation of mixed esters of cholesteryl dicarboxylic acids has been described [10].

Cholesteryl succinyl epoxypropionate (CSEP)

The synthesis could not be performed by Maerker's procedure [12]. The method was modified by use of a catalyst.

Cholesteryl hydrogensuccinate (0.1 mol; 48.6 g) was dissolved in 200 cm^3 of chloroform then neutralized with 1.0 mol (5.6 g) of KOH dissolved in 80 cm^3 of ethanol. The solution was precipitated by pouring into 1500 cm^3 of acetone. After filtration and drying, 54 g of cholesteryl potassium succinate was obtained. It was mixed with 80 g (1 mol) of epichlorhydrin and 0.001 mol of benzyl trimethylammonium chloride as catalyst. The mixture was kept at reflux for 30 min and then filtered. The filtrate was washed by water to be chloride-free; the excess of epichlorohydrin was removed by vacuum evaporation. The crude cholesteryl succinyl glycidylether was five times recrystallized from ethanol. Yield was 72% (38 g).

Cholesteryl glutaryl glycidylester (CGEP) and cholesteryl phtahloyl glycidylester (CPEP) were prepared similarly. Information on these products is collected in Table 1.

Table 1. Characteristic data of the studied compounds

	Epoxy content (%)	Crystalline m.p. (°C)	Smectic m.p. (°C)	Clearing point (°C)
R				
$-CH_2-CH_2-$	97.1	78	103	103
$-CH_2-CH_2-CH_2-$	98.8	76	97	97
	97.5	134	—	—
R'				
CH_3-*	99.4	105	—	—
C_4H_9*	98.1	92	96	96

* Both compounds have polymorphic modification after melting.

p-*Methxyphenyl*-p'-*oxybenzoylepoxypropyl ether MPEB*

p-Methoxyphenyl-*p'*-oxybenzoate (72 g; 0.172 mol) and 0.35 g benzyl trimethylammonium chloride were dissolved in 100 cm^3 of epichlorhydrin with continuous stirring at 70°C. NaOH (6.4 g; 0.16 mol) in 20% aqueous solution was added dropwise to the solution for 2 hr then the mixture was kept at 70°C for another hour. After cooling, the organic phase was separated and washed with 50 cm^3 of distilled water. Epichlorhydrin was removed by vacuum evaporation at a temperature not higher than 50°C. The residue was dissolved in a 1:2 mixture of butanol–toluene and stirred at 30°C for 1 hr in the presence of 20% solution of 1.4 g (0.035 mol) of NaOH. The organic phase was then washed by distilled water several times to neutrality. After vacuum evaporation, the organic residue was recrystallized three times from methanol. Yield was 62% (35 g).

p-Butoxyphenyl-*p'*-oxybenzoyl epoxypropyl ether (BPEP) was prepared similarly. Data for these compounds are also presented in Table 1.

It should be noted that Schleier *et al.* [13] synthesized some polymers containing a rigid core in the side chain but did not study their mesomorphic properties.

Polymerization

CSEP (2 g) was dissolved in 2 cm^3 of benzene and an ethereal solution of boron trifluoride etherate at 1.5×10^{-2} mmol/cm^3 concentration was added. The mixture was kept at 20°C for 24 hr. The system was viscous and so it was diluted with benzene before precipitation in methanol. Yield was 70% (1.4 g). Some of the monomers could be transformed into higher molecular polymers by using $FeCl_3$+propylene oxide as polymerisation catalyst [21].

Differential scanning calorimetry (DSC)

DSC thermograms were recorded by a Du Pont 910 DSC instrument. The initial and peak temperatures of the endothermic effects and the areas under peaks were considered. The peak areas were calibrated using high-purity indium.

Polarization light microscopy

A Zeiss Polmi A polarization microscope equipped with a Boetzius-type thermostated stage was used. For the texture studies, pictures were taken with a Rathenon 10/0.2 objective and MF 6.3 microprojector to Fortepan 50 film at various temperatures.

Infra-red spectroscopy

Spectra were recorded by a Perkin–Elmer 580 B spectrograph in KBr pellets or in CCl_4 solutions. Differential spectra were obtained by means of the on-line computer of the instrument.

Gel permeation chromatography

The molecular mass distribution was determined with tetrahydrofuran mobile phase on Stiropor gel colum. Methods of data processing have been reported [14].

X-ray diffractometry

The X-ray diffraction measurements were performed using the 5-GeV synchrotron (VEP-4) of the Institute of Nuclear Physics at the Novosibirsk Division of the Academy of Sciences of U.S.S.R.

A 0.1-mm wide beam was selected from the radiation by a Si monocrystal and it was sent to the sample of 1.2 mm in thickness. The primary radiation was eliminated from the transmitted beam and the diffracted intensitites were measured by a linear detector, collecting the intensity informations into 1024 channels in the range 2θ = 4 to 28°. The used wavelength was 64 pm. The temperature of samples was regulated by a heated Al-block to an accuracy of ± 1 K. For the primary radiation, the sample was encased by two Be windows 0.1 mm thickness. Intensities of the scattered radiation were recorded at an exposure time of 60 sec and processed by an ODRA computer, recording 280 to 540 impulses as a maximum for the channels. The diffractograms were smoothed, fitting third-degree polynoms in nine points each by the least squares method thus reducing the number of data points to 1/4. In this way, the ratio of the number of impulses to the channel noise could be diminished from 20–30 to 6–8. The presented diffractograms are based on these continuous lines drawn through the median values of the scattered points obtained by the above procedure.

RESULTS

Degrees of oligomerization calculated from GPC and clearing points are presented in Table 2. In spite of the absolute values of molecular masses (calibrated with epoxide compounds), it is clear that degrees of oligomerization of the synthesized products are between 4 and 8 as expected. Elevation in clearing temperature is considerable, especially for aromatic polymers containing rigid core when using $FeCl_3$ + propylene oxide catalyst. X-ray diffractograms of poly-CSEP and poly-MPEP are shown in Figs 1 and 2, corresponding to an amorphous material in both cases. The following indentity periods were obtained corresponding to the diffuse peak maxima: 5.57 and 5.31 nm for poly-CSEP, 4.20 and 4.36 for poly-MPEP. The first values refer to room temperature, the second to the isotropic state of the material (165 and 145°C, respectively). These values agree with those of other polymers having similar side chains [14–16].

Table 2. Degree of polymerization and clearing point of oligomers prepared using boron trifluoride etherate* and $FeCl_3$ + propylene oxide catalyst†

Oligomers	$\bar{P}$	Clearing point (°C)
CSEP*	4 – 8	160
CGEP*	5 – 9	205
CGEP*	4 – 8	170
MPEP	5 – 6	162
BPEP*	5 – 6	132
CSEP†	9 – 11	208
MPEP†	11 – 12	300
BPEP†	11 – 12	285

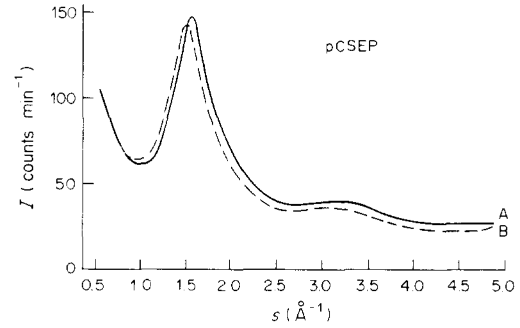


Fig. 1. X-ray diffractograms of poly(cholesteryl succinyl epoxypropionate) at room temperature (A) and at 165°C (B).

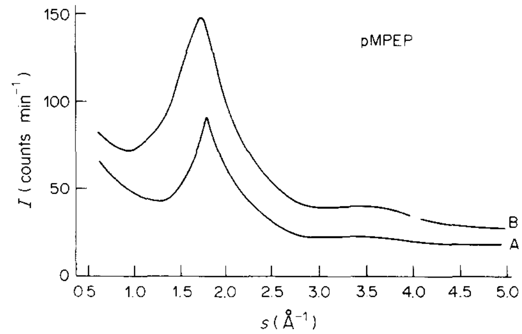


Fig. 2. X-ray diffractograms of poly(p-methoxyphenyl-p'-oxybenzoyl epoxypropyl ether) at room temperature (A) and at 145°C (B).

Polarization microphotograph are shown in Fig. 3. Optical anisotropy of the oligomers is apparent but the textures are not definitely identical with the standard [17] textures. At the clearing point, disappearance of the optical anisotropy occupies a relatively wide temperature range (about 10 K) compared with conventional mesomorphic materials. Values in Table 2 refer to the temperatures at which the completely dark picture area is attained.

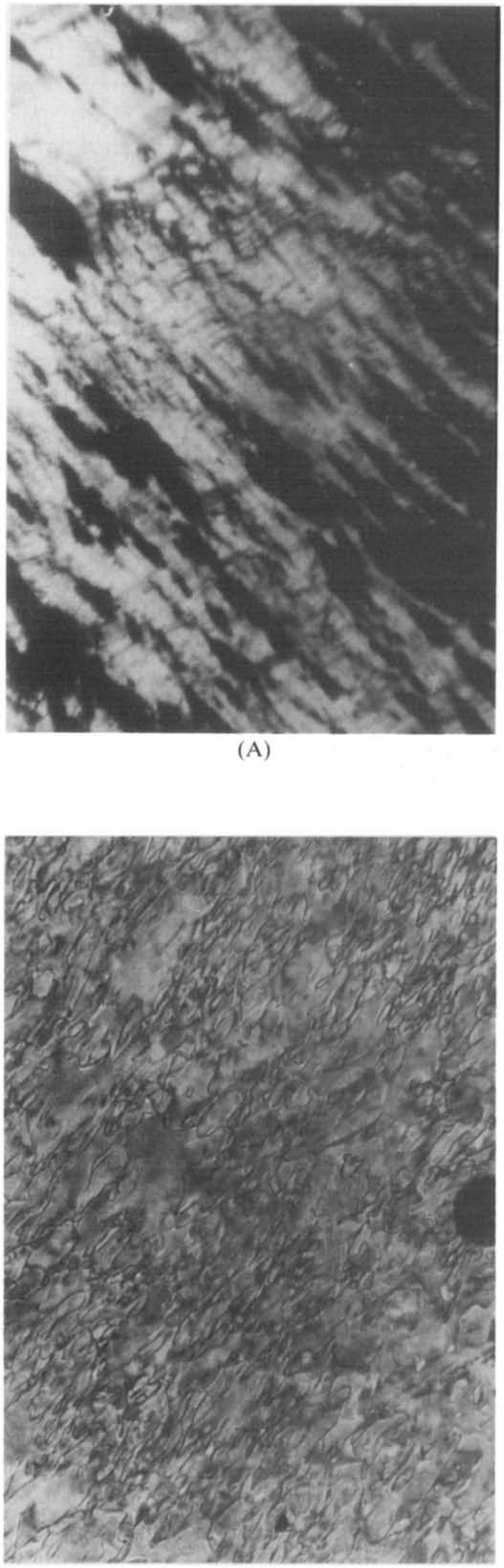
Melting DSC traces of oligomers are shown in Figs 4 and 5. Both melting and clearing process are accompanied by endotherms. The clearing point measured by optical methods corresponds to the enthalpy maximum on the DSC record.

An interesting exothermic process was observed for the CSEP oligomer. Its latest heat was 170 J/g though no indication of chemical reaction was revealed. It was demonstrated by the i.r.-spectra of the initial and the thermally treated sample in Fig. 6. A derivatogram was also recorded with poly-CSEP where the exothermic effect was well shown again but without mass change (Fig. 7). In a repeated thermal treatment, this exothermic process was not observed. Even at the first melting of the higher-molecular poly-CSEP, a strong exothermic latent heat was observed. No explanation has been found.

DISCUSSION

Clearing points and glass transition temperatures (T_g) of polymers containing identical rigid core but different main chains and different length of spacer are collected in Table 3.

The Table clearly shows that T_g is dramatically reduced while the clearing point is raised for



(A)

(B)

Fig. 3. Polarization microphotographs of poly(cholesteryl succinyl epoxypropionate) (A) and poly(p-methoxyphenyl-p'-oxybenzoyl epoxypropyl ether) (B). $\bar{P}$ in both cases is about 4 to 8. Magnification is 340 times, temperature 110°C.

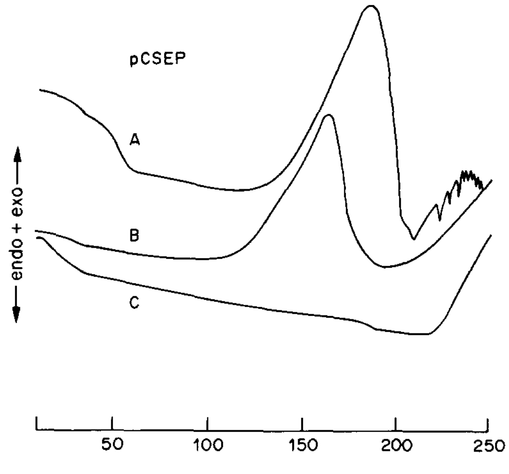


Fig. 4. DSC thermograms of poly(cholesteryl succinyl epoxypropionate). (A) Oligomer of $\bar{P}$ = 8 to 9. (B) Oligomer of $\bar{P}$ = 4 to 8. (C) As (B) in the second melting.

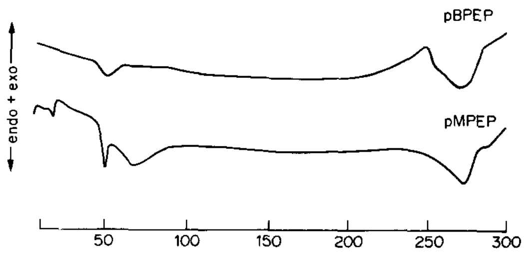


Fig. 5. DSC thermograms of poly(methoxyphenyl-p'-oxybenzoylepoxypropyl ether) and poly(butoxyphenyl-p'-oxybenzoyl epoxypropyl) ether.

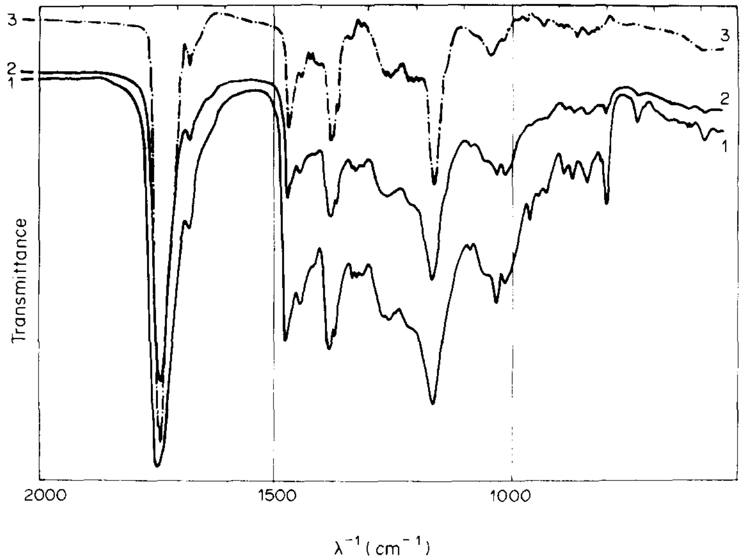


Fig. 6. I.R.-spectra of poly(cholesteryl succinyl epoxy-propionate). (1) Original; (2) after thermal treatment at 150°C; (3) difference of (1) and (2). Sample in KBr pellet.

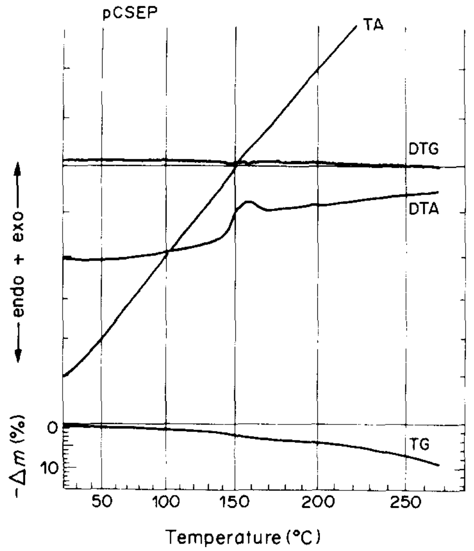


Fig. 7. Derivatogram of poly(cholesteryl succinyl epoxy-propionate). $\bar{P}$ = 4 to 8.

polymers having poly(ethylene oxide) main chain as compared to the acrylate polymers with short spacer. With identical main chain, omission of the spacer raises the clearing point markedly but there is an increase in T_g. By reducing the chain length of poly(ethylene oxide), the clearing points approach those of polymers with polyacrylate main chain containing -O-CH_2-CH_2-O- spacer.

Clearing points of all polymers are considerably higher than that of the monomer. The presence of the main chain increases the clearing point of the mesomorphic system and consequently extends the thermal stability of the ordered structure to the collective system. It is especially marked for the poly(ethylene oxide) chain where the increasing chain length may raise the clearing ponit by 100 K as compared to that of the monomer (T_c): values of T_c for poly-MPEP, MPEP, poly-BPEP and BPEP are 200, 105, 185 and 96°C respectively. The flexible main chain apparently suppresses the vibration of the rigid core in the direction perpendicular to the main axis. All the main chains hinder the crystalline arrangement of the rigid cores.

It is interesting that no crystalline system was observed with blends of low-molecular oligomers. The "polymeric" character of oligomers seems to be associated with length exceeding the mean segmental length. Polymeric phenomena will appear in any system where the length of the molecular chain exceeds the distance of persistence of the molecule [19]. The latter is quite small in poly(ethylene oxide) due to the high chain mobility, in fact, not longer than the average chain length of the oligomer blends of $\bar{P}$ = 4 to 8 used in this work.

Unfortunately, no direct data could be obtained about polymers with a polysiloxane main chain and containing no rigid core; the effect of a main chain much more flexible than that of poly(ethylene oxide) could not be compared. It should be noted, however, that instability phenomena are expected in polysiloxanes due to their irreversible changes in the frozen state of the copolymers because of the known bonding rearrangements as concluded from the data of Frenzel and Rehage [20].

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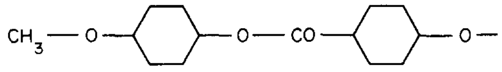
Table 3. Characteristic data of polymers with various main chains containing spacers (S) of various lengths

Polymers	Type of main chain	Clearing point (°C)	T_g (°C)
CA	-CH$_2$-CH- | CO | O | Ch	220	130
CVS	-CH$_2$-CH- | O | CO | S-CO-O-Ch	190	45
CSEP	-CH$_2$-CH-O- | CH$_2$ | O-CO-S-CO-O-Ch	208	10
MPAB	-CH$_2$-CH- | CO | R	250	110
MPAEB	-CH$_2$-CH- | CO | O-S-R	116	62
MPEP	-CH$_2$-CH-O- | CH$_2$ | R	300	12
BPAP	-CH$_2$-CH- | CO | R′	320	190
BPAEB	-CH$_2$-CH- | CO | O-S-R′	154	30
BPEP	-CH$_2$-CH-O- | CH$_2$ | R′	285	10

CA = cholesteryl acrylate; CVS = cholesteryl vinyl succinate; CSEP = cholesteryl succinyl epoxypropionate; MPAB = methoxyphenyl acryloyloxybenzoate; MPAEB = methoxyphenyl acryloyloxy ethoxybenzoate; MPEP = methoxyphenyl epoxipropionate; BPAB = butoxyphenyl acryloyloxybenzoate; BPEP = butoxyphenyl epoxypropionate; BPAEB = butoxyphenyl acryloyloxy ethoxybenzoate.

R :



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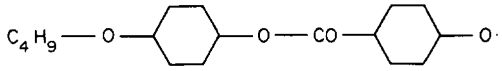
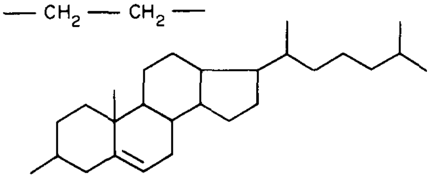


S : — CH_2 — CH_2 —

Ch :



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