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EFFECT OF MOLECULAR MASS ON THE MELTING TEMPERATURE, ENTHALPY AND ENTROPY OF HYDROXY-TERMINATED PEO

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Abstract

This paper studies the effect of molecular mass on the melting temperature, enthalpy and entropy of hydroxy-terminated poly(ethylene oxide) (PEO). It aims to correlate the thermal behaviour of PEO polymers and their variation of molecular mass (MW). Samples ranging from 1500 to 200,000 isothermally treated at 373 K during 10 min, were investigated using DSC and Hot Stage Microscopy (HSM). On the basis of DSC and HSM results, melting temperatures were determined, and melting enthalpies and entropies were calculated. Considering the melting temperatures, it was found that the maximum or critical value of MW was found around 4000, and then these remain almost constant. This behaviour was interpreted assuming that lower MW fractions (MW<4000) crystallize in the form of extended chains and higher MW fractions (MW>4000), as folded chains. The melting enthalpies showed a scattering effect at least up to MW 35,000. It was difficult to obtain any relationship between melting enthalpies in J g^{-1} and MW. These variations seem to be of statistical nature. Corrected enthalpy data on a molar basis (kJ mol^{-1}) exhibited a linear relationship with MW. Considering the solid–liquid equilibrium, the melting entropies (in kJ mol^{-1}) were calculated. These values were more negative as compared with molar enthalpy increases. It was explained because the changes in melting temperatures are much smaller than those observed in the enthalpy values. Linear relationship between enthalpies and entropies as a function of MW was deduced.

Keywords: DSC, melting enthalpies, melting temperatures, molecular mass, PEO polymers

Introduction

Hydroxy-terminated poly(ethylene oxide)s (PEO) are a group of water-soluble synthetic polymers obtained by catalytic condensation of ethylene oxide and water [1–4].

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The general formula of these compounds corresponds to $HO(CH_2–CH_2O)_nH$, where n represents the average number of oxyethylene groups ($–OCH_2–CH_2$) or the degree of polymerization. PEO polymers are available in a wide range of nominal molecular masses (200 to several millions), with different functional end groups and several commercial trade names. The hydroxy-terminated group of these polymers are also named poly(ethylene glycol)s (PEG). Already in the sixties, basic studies on PEG conformation, crystalline structure and thermal behaviour of different modifications were performed [1, 2].

PEO are semicrystalline polymers which, in the solid state, contain both amorphous and crystalline regions in varying proportions depending upon the synthesis and their thermal history [1–10]. In the amorphous phase, the polymer chains have a random orientation. In the crystalline regions, PEO molecules exist as a double parallel helix [2]. The helices are arranged as plate-like structures known as lamellae from which the hydroxyl end groups are rejected onto the surfaces [9]. It has been previously reported since the early 1960s that PEO polymer forms helical structures [2]. Thus, X-ray, NMR and IR results [2, 4] support that the structure consists in seven monomer units ($–OCH_2–CH_2$) with two turns per repeat unit. Scanning tunneling microscopy measurements on PEO adsorbed on graphite has confirmed the above structural model (no structure differences using PEO molecular masses 14200 and 21800), being proposed a hierarchy of superhelical structures accounted for the observed microscopy images [11]. The chains within the lamellae may exist as extended or folded chains, depending on the molecular mass (MW) of PEO [10]. The folded chains are considered metastable as compared with the extended ones. The lamellae are, in turn, arranged in spherical structures with fine radiating branches, called spherulites [4, 6, 7]. The physical properties of these polymers are closely related to the thickness and distribution of lamellae, the crystallinity and the size of distribution of spherulites, and the content and distribution of short side chains.

The valuable applications of these polymers justify the high number of studies. It could be mentioned as relevant examples how they are used as carriers in the pharmaceutical technology for the manufacture of the so-called ‘solid dispersions’ (PEG molecular mass ranging from 1500 to 200 000), which are prepared to enhance the dissolution rate of poorly water-soluble drugs by dispersing the drug in this kind of carrier or polymer matrix [12–14]. The improvement in drug dissolution rate is dependent for the same drug-carrier ratio on the elaboration conditions [13]. On the other hand, grafting polymeric dispersants such as PEG, to powders is an attractive method for processing ceramic powders [14–16]. Some of the many advantages include improved colloid stability and more precise control of dispersant quantity, resulting in an enhanced uniformity of ceramic particle compacts. Grafting PEG on silica [14], alumina powders [16] and other oxides [12] has already been reported. Other important practical applications (chromatography, etc.) [17], as well as the fundamental interest of these materials justify all these research efforts. Recently, Zheng *et al.* [18] have used PEG and PEO polymers, both water-soluble binders, as plasticizers and lubricants for ceramic extrusion applications.

In all the aforementioned applications, it is very important to know deeply the thermal behaviour of this kind of polymers, which is influenced, in turn, by the chain length and molecular mass of the polymer used. Several classical studies on the melting of very low molecular mass PEO samples have been made [1–10]. Thus, it has been evidenced that the thermal history of PEO plays a significant role in the results when these polymers are investigated by thermal analysis methods. The effect of molecular mass on the melting transition and the relation of crystallization temperature to fusion have been studied mainly using dilatometry and small-angle X-ray scattering. The end group effect of PEO with low molecular mass on fusion has also been reported [19]. Systematic research on the melting behaviour of low molecular mass PEO fractions has been done using differential scanning calorimetry (DSC) [10, 20, 21] and the thermoanalytical method has been applied to measure the entropy of fusion [22]. Thus, it was reported that PEO of molecular mass near 6000 has two melting transitions [20]. It was also reported after a thermal study by DSC that samples of PEO with molecular mass 4000 show two endothermic melting points, and an exothermic recrystallization peak between them [21]. This observation is in agreement with the earlier results of small-angle X-ray scattering and density measurements [1], which indicated a complex morphology in such polymers.

The effect of annealing on the thermomechanical properties of PEO [23], melt viscosity and thermal properties of PEO fractions and blends (1500−40 000), have been also investigated [24]. It should be noted that Kambe [21] has further confirmed the dependence of DSC traces of PEO on the previous thermal history and, consequently, the values of melting enthalpies. Costagliola *et al.* [24] reported an apparent enthalpy of fusion, calculated from the DSC curve, about 40 cal g^{-1} (166.6 J g^{-1}). These authors claimed that this value does not change with varying molecular mass, thus indicating that the degree of crystallinity is nearly constant for fractions lying in the range of MW examined (10^3 to 20 000). Presence of peroxides, a by-product often associated with this kind of polymers [25, 26], can contribute to the formation of degradation products after production of the melt, and hence will influence the thermal properties. In particular, it has been recognized [3] that poly(ethylene oxide) is particularly useful for studies on the properties of crystalline polymers of low molecular mass (1000–20 000), and samples with narrow molecular mass distribution are readily available.

In the present work, the effect of molecular mass on the melting temperature, melting enthalpy and melting entropy of PEO polymers, ranging from 1500 to 200,000, is reported. A previous treatment on the examined samples was performed in order to eliminate the thermal history caused by processing and storage conditions, which is the origin of important variations in the final results obtained and several discrepancies observed in literature [1, 3, 5, 20, 21, 24].

Experimental

PEO samples as flakes, which are applied in the pharmaceutical technology, having nominal molecular masses (MW) 1500, 4000 and 6000, were supplied by Acofar (Barcelona, Catalonia, Spain), and those ranging from 15 000 up to 200 000 provided by Serva Laboratories (Barcelona, Catalonia, Spain). These samples were used without further purification. The nominal MW of this set of PEO samples were accurately guaranteed by the suppliers after careful gel permeation chromatography and high-performance liquid chromatography measurements.

Powdered PEO samples obtained using a cutting-mill (to avoid structural alterations induced using other grinding devices) were exactly weighed (10 mg with accuracy of 0.1 mg), placed into flat-bottomed aluminium pans (45 μL), heated using a DSC Mettler equipment, model FP85, from 303 to 373 K at a heating rate of 10 K min^{-1} and isothermically treated at 373 K during 10 min. Identical thermal treatment was applied to all examined specimens in order to eliminate any thermal history. After this treatment, the samples were cooled at room temperature. Next, DSC measurements were performed at a heating rate of 10 K min^{-1} and melting enthalpies determined after integration of the areas under the melting DSC endotherms, following calibration with high-purity indium and using the software supplied with the equipment. Melting temperatures were determined as bottom peak temperatures (T_p), or maximum of the considered peak, and extrapolated onset temperatures (T_e), defined as the point of transition, being the point of intersection between the base line and the DSC endothermal melting effect, which gives the most reproducible value, experimentally independent of the operator [20]. The temperature at which melting started (thaw point) was determined by Hot Stage Microscopy (HSM) using a Mettler equipment, model FP82 HT and Olympus BH-2 Microscope. Samples of 0.1 mg placed on glass slides with coverglass, heated at the rate of 5 K min^{-1} were examined using this technique (triplicate runs).

Results and discussion

The melting temperatures (T_p and T_e) plotted as a function of PEO molecular mass are shown in Fig. 1. These values are in agreement with those reported by other authors [3–5, 20, 24]. It should be noted that the thaw points obtained from HSM observations were higher by 2–3°C than those determined from the DSC curves (Fig. 1), which is in accordance with previous results [5]. This fact can be associated to a) subjective estimation of melting temperatures by HSM in spite of triplicate runs carried out using this technique; b) different conditions of heat transfer using HSM (thin films respect to bulk samples studied by DSC) and c) differences in heating rate conditions as described above in experimental section.

From the results reported in Fig. 1, it can be seen that the melting temperatures show a pronounced increase with molecular mass between PEO 1500 and 20 000, after which the melting temperature determined as T_p does not rise substantially, or slightly decreases as determined by T_e data. It has been suggested [20] that this kind of hydroxy-terminated polymers exhibit a melting range which is dependent on sample source, preparation conditions and thermal history rather than a specific melting point temperature. The critical value of molecular mass was found around 4000, and then the melting temperatures remain almost constant. In accordance with other authors [20, 24], this behaviour can be interpreted assuming that the lower molecular mass fractions (MW<4000) crystallize in the form of extended chains and the higher molecular mass fractions (MW>4000), as folded chains. In the former case, the lamellar thickness is given by the chain length itself, whereas in the latter it is independent of molecular length and will depend only on the crystallization conditions [5, 24]. However, the similar curve of Fig. 1 as reported by Costagliola *et al.* [24] in a previous paper, provided only melting temperatures (T_m) obtained from maxima of the fusion endotherms (i.e., the values of T_p plotted in Fig. 1). These authors reported a plot of melting point temperatures (i.e., T_m) obtained by DSC *vs*. MW of PEO fractions, but unfortunately no scanning speed data were indicated in their paper [24]. A more realistic situation can be assessed in the present paper considering T_e data instead of T_p. The slight decrease observed in T_e plot (Fig. 1) can be assigned to a broader DSC endothermal peak obtained as increasing PEO molecular mass, which is an indication of the variations progressively observed in the crystallinity of this kind of polymer samples [20].

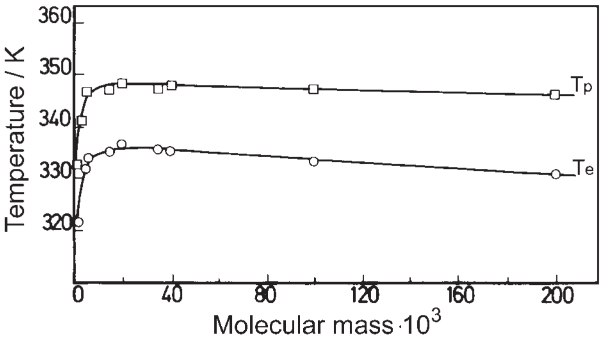

Fig. 1 Plot of melting temperatures of PEO samples, determined as peak (T_p) or extrapolated (T_e) temperatures from DSC measurements (heating rate 10 K min^{-1}), as a function of PEO molecular mass

On the other hand, the values of melting enthalpies in J g^{-1} (Fig. 2) show a trend to increase as increasing the molecular mass, with a maximum at PEO 6000, and decreased continuously up to 35 000 as illustrated in Fig. 2. This last sample shows a value similar to 1500. Other relative maximum is observed at molecular mass (MW) 40 000 followed by a decrease, reaching at 200 000 a value rather lower than that observed at 1500. These results showed a scattering effect at least up to MW 35 000 and the difficulty to obtain a relationship between melting enthalpies in J g^{-1} and MW, in accordance with previous works [10, 20]. These variations seem to be of statistical nature. However, a plot of the experimental enthalpy data (ΔH_m) on a molar basis (kJ mol^{-1}) shows a linear relationship with MW and, hence, with the degree of polimerization *n* in the general formula of outlined PEO compounds described as $HO(CH_2–CH_2O)_nH$. The increase of enthalpy in kJ mol^{-1} as increasing MW is not surprising, but expected. The corresponding regression equation is:

$$-\Delta H_m = -55.836 - 0.2688\ \text{MW}$$

and coefficient of regression

$$r=-0.999(4) \text{ for MW} <=10^5.$$

Considering the solid–liquid equilibrium, then $\Delta G_m=\Delta H_m-T_m\Delta S_m=0$, where the symbols have the usual meaning in chemical thermodynamics, the entropy of melting is $\Delta S_m=\Delta H_m/T_m$. If it is assumed that T_m is approximately the same as T_e, the ΔS_m values can be readily calculated from the above results (Fig. 1). As expected, ΔS_m in kJ mol^{-1} is more negative as ΔH_m increases because the changes in T_e values are much lower than that observed in ΔH_m. A similar linear relationship between ΔS_m and MW, as shown in Fig. 2, can thus be deduced. In that case, the linear regression is as follows:

$$-\Delta S_m=-0.853-7.6\cdot10^{-4} \text{ MW, with } r=-0.999(2) \text{ for MW}<=10^5.$$

According to several theoretical approaches, the melting temperatures of PEO samples can be predicted. For instance, the melting temperatures (T_m) for different PEO samples can be reasonably predicted using the Flory relation [27] $(1/T_m)-(1/T_m^0)=2R/(H_f n)$, where T_m^0 is an equilibrium melting temperature of the polymer with infinite molecular mass, H_f is the molecular heat of fusion per chain and n the degree of polymerization. Assuming that H_f is 620±50 cal mol^{-1} or 2.5833 kJ mol^{-1} [5] and T_m^0=70°C (343 K), according to Godovsky *et al.* [5], then melting temperatures of PEO polymers with different MW can be calculated using the aforementioned equation.

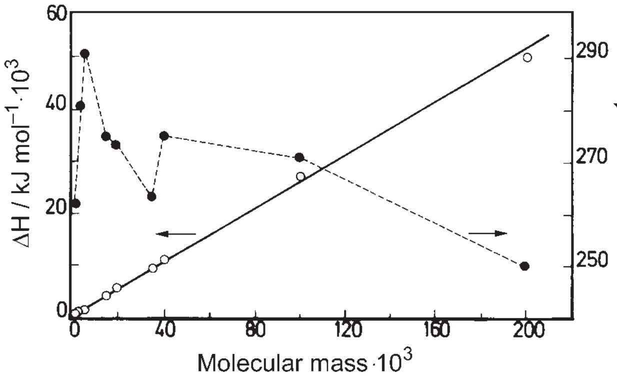

Fig. 2 Plot of melting enthalpies determined from DSC measurements, following calibration with high-purity indium, in J g^{-1} and kJ mol^{-1} of PEO samples, as a function of PEO molecular mass

After some of these calculations, the results have shown differences T_e(experimental)–T_e(calculated) ranging from –1 K, in the case of PEO 1500, up to a maximum of –10 K, in the case of PEO with MW=10^5. These differences are slightly lower if the value T_m^0=68.6°C (341.6 K) is considered, a value experimentally obtained for PEO of MW=$6\cdot10^6$ as noted in a previous work [29]. However, the most reliable value for T_m^0 is obtained from extrapolation of data for samples of low crystallinity and high crystallization temperature, having been found a value of T_m^0=76°C (349 K) considered the thermodynamic melting point of PEO [29]. It is worth indicating that using this value to recalculate melting temperatures, following the procedure described above, produced important differences as compared with the present T_e results determined from DSC measurements.

On the other hand, there are some discrepancies comparing the melting enthalpies calculated from DSC curves (Fig. 2) and literature values. It will be discussed in the next paragraphs considering previous contributions in this subject. In an earlier paper [5], direct calorimetric determinations of the heat of fusion of PEO fractions above MW=600 indicated a value of 41±1 cal g^{-1} (170.8 J g^{-1}), which was considered molecular mass independent. A value of 45 cal g^{-1} (187.5 J g^{-1}) was reported for completely crystallized PEO samples [8]. Costagliola *et al.* [24] reported a value of 'apparent enthalpy of fusion', calculated from DSC, at ca. 40 cal g^{-1} (166.6 J g^{-1}). These authors claimed that this value does not change with varying molecular mass, thus indicating that the degree of crystallinity is nearly constant for fractions lying in the range of MW examined (10^3 to 20 000) [24]. Buckley and Kovacs [10] reported a value of 47.0 cal g^{-1} (195.8 J g^{-1}) obtained for a perfect crystal of infinite dimensions. However, Beaumond *et al.* [30] calculated that the enthalpy of fusion of a 100% PEG crystalline material of MW= 4000 is 51.5 cal g^{-1} (214.6 J g^{-1}), with a melting temperature of 336 K. These data have been used as standard values by many workers to estimate the degree of PEG crystallinity.

It should be noted that some attempts have been made to modify the Flory equation [27]. Beech *et al.* [31] modified this equation taking into account the lamellar crystals of the polymer of a given thickness chain units, the end interfacial free energy of the lamellar crystal (G_e), the thermodynamic melting point T_m^0=76°C (349 K) [29], the enthalpy of fusion of bulk polymer per chain unit H_f=2 kcal mol^{-1} (8.3 kJ mol^{-1}) [30] and G_e in the range 1–5 kcal mol^{-1}. With these corrections, the melting temperature predictions for PEO polymer with MW>10^3 can be improved. However, other authors [10] used the theory of Flory and Vrij [31] to derive analytical expressions to predict melting temperature of low molecular mass PEO samples ranging from 3000 to 10 000.

Finally, the present authors want to remark that there are several experimental factors that influence the thermal behaviour observed in PEO polymers as studied by DSC. For instance, according to previous reports [10, 20], the heat of fusion and melting points of PEG samples varied with scanning speed, especially for the lower PEG fractions. The thermal history may determine both the degree of crystallinity and the crystal form of the PEG, as shown by changes in the heat of fusion and melting temperatures, respectively. An increase in the melting temperatures with scanning speed has been reported for several compounds, for instance PEG 6000, according to previous results [10], and commonly used melting point standards [20, 32]. This fact may be due to the finite melting rate of the crystals, thus leading to the measured temperature rising at a faster rate during the lag period at higher scanning speeds. Further experimental work would be necessary to reach most plausible reasons of such a thermal behaviour, in particular concerning PEO polymers.

Conclusions

The effect of molecular mass on the melting point, melting enthalpies and melting entropies of hydroxy-terminated poly(ethylene oxide) (PEO) samples has been studied. Samples ranging from 1500 to 200 000 were investigated using DSC and HSM. A previous thermal treatment on the samples was performed in order to eliminate the thermal history caused by processing and storage conditions, which is the origin of important variations in the results of previous reports. On the basis of DSC and HSM results, melting temperatures were determined and melting enthalpies and melting entropies were calculated. According to the results of melting temperatures of these polymers, it was found that the critical value of molecular mass (MW) is around 4000, and then the melting temperatures remain almost constant. This behaviour was interpreted assuming that the lower molecular mass fractions (MW<4000) crystallize in the form of extended chains and the higher molecular mass fractions (MW>4000), as folded chains.

On the other hand, the melting enthalpies showed a scattering effect at least up to MW 35 000 and the difficulty to obtain a relationship between melting enthalpies in J g^{-1} and MW. These variations seem to be of statistical nature. However, corrected enthalpy data on a molar basis (kJ mol^{-1}) showed a linear relationship with MW and, hence, with the degree of polymerization of the studied PEO polymers. Considering the solid–liquid equilibrium, the melting entropies were calculated. These values, in kJ mol^{-1}, are more negative as compared to molar enthalpy increases. It is explained because the changes in melting temperatures are much lower than those observed in enthalpy values. Linear relationship between enthalpies and entropies as a function of MW was deduced. The values of these thermodynamic parameters were discussed taking into account previous literature relationships of equilibrium melting point of PEO polymers, the effect of molecular mass and some corrections to predict melting points, and other experimental factors, such as the scanning rate. In summary, the present paper attemps to correlate the thermal behaviour of PEO polymers and their variation observed in MW. Further experimental work would be necessary to reach most plausible reasons for such a thermal behaviour exhibited by these polymers, in particular considering the effect of different PEO molecular mass fractions.

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References

1 J. P. Arlie, P. A. Spegt and A. E. Skoulios, Makromol. Chem., 99 (1966) 160.
2 H. Tadokoro, Macromol. Rev., 1 (1966) 119.
3 D. R. Beech, C. Booth, D. V. Dogson and I. H. Hillier, J. Polym. Sci.: Part A-2, 10 (1972) 1555.
4 F. E. Bailey and J. V. Koleske, Polyethylene oxide, Academic Press, New York, USA 1976.
5 Yu. K. Godovsky, G. L. Slonimsky and N. M. Garbar, J. Polym. Sci. Part C, 38 (1972) 1.

6 M. Mihailov, E. Nedkov and I. Goshev, J. Macromol. Sci. Phys., B15 (1978) 313.

7 R.C. Allen and L. Mandelkern, J. Polym. Sci. Polym. Phys. Ed., 20 (1982) 1465.

8 L. Mandelkern, Crystallization of Polymers, McGraw–Hill, New York 1964.

9 A. J. Kovacs, A. Gonthier and C. Straupe, J. Polym. Sci., 50 (1975) 283.

10 C. P. Buckley and A. J. Kovacs, Coll. Polym. Sci., 695 (1976) 695.

11 R. Yang, X. R. Yang, D. F. Evans, W. A. Hendricks and J. Baker, J. Phys. Chem., 94 (1990) 6123.

12 W. L. Chiou and S. Riegelman, J. Pharm. Sci., 60 (1971) 1281.

13 J. L. Ford, A. F. Stewart and J. L. Dubois, Int. J. Pharm., 26 (1986) 11.

14 H. Hommel, A. P. Legrand, P. Tougne, H. Balard and E. Papirer, Macromol., 17 (1984) 1578.

15 M. L. Green, T. Kramer, M. Parish, J. Fox, R. Lalanandham, W. Rhine, S. Barclay, P. Calvert and H. K. Bowen, Advances in Ceramics Vol. 21, Ceramic Powder Science and Technology, The American Ceramic Society, Westerville, USA 1987.

16 M. L. Green, W. E. Rhine, P. Calvert and H. K. Bowen, J. Mater. Sci. Lett., 12 (1993) 1425.

17 Yu. S. Lipatov and C. M. Sergeeva, Adsorption of Polymers, J. Wiley and Sons, New York, USA 1974.

18 J. Zheng, J. S. Reed and S. K. Verma, Am. Ceram. Soc. Bull., 73 (1994) 61.

19 M. J. Fraser, D. R. Cooper and C. Booth, Polymer, 18 (1977) 852.

20 D. Q. M. Craig and J. M. Newton, Int. J. Pharm., 74 (1991) 33.

21 Y. Kambe, Polymer, 21 (1980) 352.

22 A. M. Afifj-Effat and J. N. Hay, J. Chem. Soc. Faraday Trans., 2 (1972) 656.

23 E. Alfthan and A. de Ruvo, Polymer, 16 (1975) 692.

24 M. Costagliola, R. Greco and A. Martuscelli, Polymer, 19 (1978) 860.

25 J. L. Ford, Pharm. Acta Helv., 59 (1984) 280.

26 S. M. Chatham, S. T. P. Pharm., 3 (1987) 575.

27 P. J. Flory, J. Chem. Phys., 17 (1949) 223.

28 J. N. Hay, M. Sabir and R. L. T. Steven, Polymer, 10 (1969) 187.

29 D. R. Beech and C. Booth, Polymer Lett., 8 (1970) 731.

30 R. H. Beaumont, B. Clegg, G. Gee, J. B. M. Herbert, D. J. Marks, R. C. Roberts and D. Sims, Polymer, 7 (1966) 401.

31 P. J. Flory and A. Vrij, J. Am. Chem. Soc., 85 (1963) 3548.

32 M. D. Tuladhar, J. E. Carless and M. P. Summers, J. Pharm. Pharmacol., 35 (1983) 208.