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Relationship between conformation and enthalpy or volume relaxation in polycarbonate

N. Heymans[a,*], B. Dequenne[b]

[a]Physique des Matériaux de Synthèse 194/08, Université Libre de Bruxelles, B-1050 Bruxelles, Belgium
[b]51, rue Flore, F-76600 Le Havre, France

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Abstract

Conformational changes are observed during sub-T_g annealing of solution-cast films of BPA–polycarbonate by following changes in the conformationally sensitive IR aromatic breathing band at 1600 cm^{-1}. The rate of conformational relaxation is compared with published data on enthalpy and volume relaxation on the same polymer. The relaxation rates and timescales converge in the immediate vicinity of T_g, but diverge at temperatures below $T_g - 15$ K and conformational energy only accounts for a very small fraction of observed enthalpy relaxation. The results suggest that a single process is active in volume and conformational relaxation and that at least two processes contribute to enthalpy relaxation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: FTIR; Polycarbonate; Annealing

1. Introduction

A preliminary investigation by FTIR spectroscopy of conformational changes occurring in BPA–polycarbonate during thermomechanical treatments [1] showed that during sub-T_g annealing, shifts from *trans–cis* (t–c) to more stable *trans–trans* (t–t) conformations occur. Similar modifications were observed during annealing of plastically deformed samples, although not during room-temperature aging, which appeared to produce a narrowing of the distribution of conformations around t–c and t–t conformations. In this paper, annealing is investigated more thoroughly and a correlation is attempted between the change in t–c and t–t populations and structural relaxations measured by independent methods such as volume and enthalpy relaxations.

2. Experimental

2.1. Thin film preparation

The material used was commercially available Makrolon® (Bayer) in a 2-mm-thick sheet. This sheet was used because it was the same material as used previously in investigations of thermomechanical effects in this laboratory [1–5]. Thin films were prepared by casting a 6% solution of PC cuttings in 1,2-dichloroethane onto glass slides and dried at room temperature for 24 h in a ventilated chamber. The films were then heat treated at 165°C for 2 h to ensure total elimination of residual solvent, to relax any internal stresses, which may have resulted from the casting process and to obtain a reproducible initial state for all samples. The film thickness was controlled by spreading a measured volume of solution over a known surface; by this method film thicknesses ranging from 20 to 50 μm could be obtained from a 6% solution, which is close to the solubility limit. As indicated below, film thicknesses of approximately 80 μm are required to obtain an appropriate absorbance for the investigated infrared band. In a first attempt to obtain thicker films, a second layer was deposited on the first after solvent evaporation; this method was abandoned since the films obtained were hazy, indicating partial crystallization, which was confirmed by DSC. Finally, two films of 40 μm in thickness were superposed to obtain the required absorbance. This method has the added advantage of eliminating the interference fringes that appear when thin films are too regular; these fringes tend to obscure small differences between spectra.

2.2. Annealing treatments

After preliminary heat treatment at 165°C, the samples were transferred to a specially designed environmental

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* Corresponding author. Tel.: +32-2-650-2776; fax: +32-2-650-2766.
E-mail address: nheymans@ulb.ac.be (N. Heymans).

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chamber fitted in the sample compartment of a Perkin–Elmer 1725X FTIR spectrometer. During the heat treatment and transfer, samples were placed in a sample holder having high thermal inertia designed to avoid indirect quenching effects, which have been observed previously to lead to considerable data scatter. Special care was taken to leave the film stress-free. Annealing was carried out at temperatures ranging from 125 to 135°C. These temperatures are well within the annealing range, which extends from T_g (approximately 145°C) to approximately $T_g - 50$ K. The upper limit was chosen in order to obtain measurable modifications of the selected absorption band and the lower limit in order to reach equilibrium within a reasonable time (a week or so). The temperature of the chamber dropped by about 5°C after transferring the sample; the prescribed temperature was recovered after approximately 2 min. This time was taken as the start of annealing.

2.3. Infrared measurements

In previous work, conformational changes were monitored using the C=O stretching absorption at 1775 cm^{-1}, which was identified by Schmidt et al. [6] as a doublet containing contributions at 1767 and 1785 cm^{-1} from t–t and t–c conformers, respectively. This band is, however, complicated by Fermi resonance and five components appear on deconvolution, casting doubt on reliability of quantitative or semi-quantitative estimates of populations of conformers using this band. In this work, the conformationally sensitive band at 1600 cm^{-1} (indicated by an arrow in Fig. 1) was investigated; this band, from in-plane stretching of the phenylene groups, contains clearly identifiable contributions from t–t and t–c conformers at 1594 and 1604 cm^{-1}, respectively. It is considerably weaker than the carbonyl stretching vibration and requires much thicker films than those used in the previous investigation. A peak absorbance of approximately 1, which is an optimal trade-off between low absorbances in the linear range of Beer's law, and high absorbances required for adequate sensitivity to small modifications, requires a film thickness of approximately 80 μm; films of appropriate thickness were prepared as indicated above.

Spectra were obtained at 4 cm^{-1} resolution; the reference spectrum was taken at the start of annealing, the following spectrum 10 min later and thereafter spectra were taken at time intervals on a logarithmic scale of ratio approximately 2. A fresh background was taken before each spectrum and 16 scans were averaged for each spectrum; this was an upper limit at short annealing times to keep scan times significantly shorter than annealing times. At longer annealing times, the number of scans could be increased; however, this produced no improvement of the quality of results, probably because of sample heating in the infrared beam: as the t–t and t–c populations are temperature-sensitive, temperature changes during the scan induce changes in the spectra, which interfere with those induced by annealing and it is therefore preferable to keep such perturbations constant by keeping the number of scans identical for all annealing times.

2.4. Data analysis

Spectra were analysed in the range 1550–1650 cm^{-1}. A linear baseline correction was applied between minima on either side of the absorption band; these minima occurred at 1626 and 1562 cm^{-1}, respectively. The reference spectrum was then subtracted from the current spectrum; a typical example of the difference spectrum thus obtained is given in Fig. 2. Notations used here are A for absorbance (left-hand axis) and A_D for absorbance difference (right-hand axis). The difference spectrum clearly shows the conformational modification (an increase in absorbance at 1594 cm^{-1}

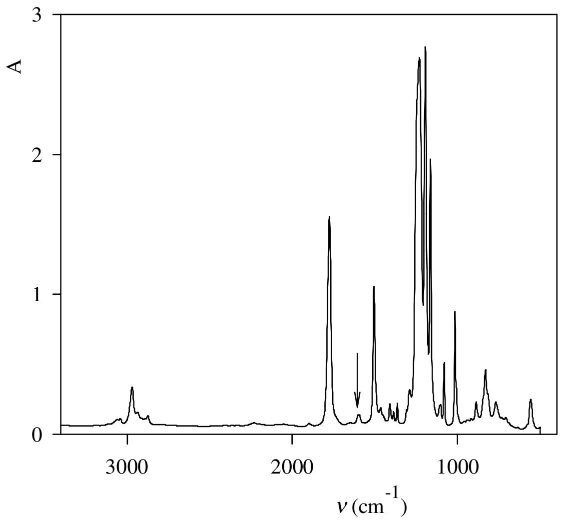

Fig. 1. Polycarbonate FTIR spectrum showing 1600 cm^{-1} band used in this investigation.

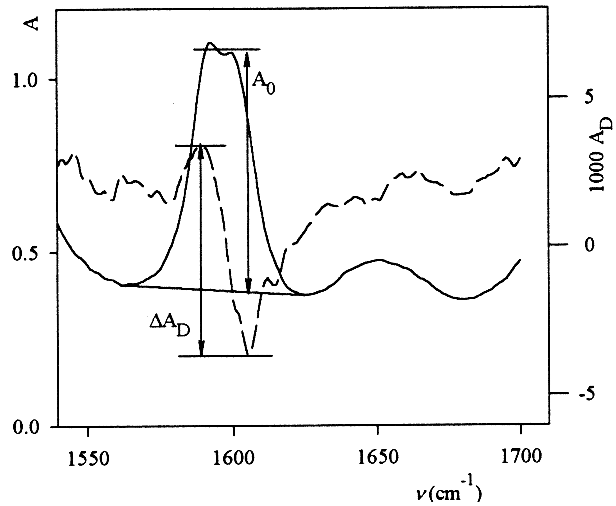

Fig. 2. Aromatic breathing band at 1600 cm^{-1} in polycarbonate. Solid line: reference spectrum at 125°C. Dashed line: difference between spectrum after 24 h at 125°C and reference. Note difference in scale.

and a decrease at 1604 cm^{-1}), which is quantified by the amount $\Delta A_D/A_0$, where ΔA_D is defined in Fig. 2 and A_0 is the average of the initial peak absorbances of the two components of the band. For a given sample, neither the slope nor the level of the baseline were sensitive to annealing. Slopes were typically -4×10^{-4} cm and fluctuations during annealing were typically of order 10^{-5} cm. When taking the difference between spectra, the major effect of any baseline changes is an offset of A_D from zero, but the effect on the measured ΔA_D is very small. The maximum contribution of baseline fluctuations to $\Delta A_D/A_0$ is estimated to be less than 0.02%. This method gave more consistent results than obtaining peak areas by curve fitting, or deconvolution, which are far more sensitive to changes in baseline shape and slope, and to noise in the data, leading to uncertainties in parameters obtained by these methods of the order of one percent, i.e. at least as large as the observed modifications. The superiority of use of difference spectra over curve fitting when investigating small changes in spectra was noted previously [1].

3. Results

3.1. Conformational changes from IR spectroscopy

The change in relative height of the difference peak during annealing is given in Fig. 3. The trends are similar to those found by densitometry or calorimetry [2,3]: at short times, the changes are not strongly temperature-dependent, but the saturation or equilibrium level is reached after longer times at lower temperatures and the relaxation amplitude increases with decreasing temperature.

The present results show a more consistent temperature dependence than the preliminary results published previously [1] although the absolute values of relative change of absorbance are considerably lower. The difference in behaviour may result from differences in film thickness or from enhancement by Fermi resonance of changes in the 1775 cm^{-1} band during annealing in the previous results. These effects will be discussed more fully below.

It was observed previously [1] that sub-T_g annealing is accompanied by shifts in population from high-energy t–c to lower-energy t–t conformations, whereas room-temperature ageing is accompanied only by a narrowing of the distribution of conformations around the local minima. This behaviour parallels that of enthalpy relaxation, which is observed on annealing whereas ageing does not affect the DSC scan. It is therefore tempting to correlate the relative change in conformational changes, measured by FTIR spectroscopy with published results on enthalpy relaxation.

3.2. Comparison with enthalpy relaxation

Enthalpy relaxation measured by DSC by Bauwens-Crowet and Bauwens [3] is plotted in Fig. 3b and the equilibrium amplitude of enthalpy relaxation is plotted in Fig. 4 together with the present FTIR spectroscopy results. The trends are similar although the present results extrapolate to zero at a lower temperature than enthalpy relaxation. This can be attributed to the lower cooling rate through the glass

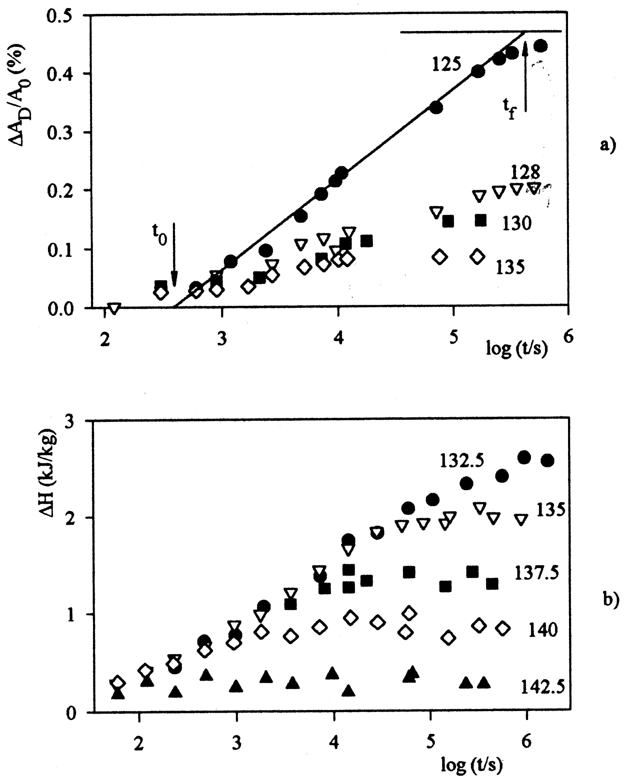

Fig. 3. (a) Change in relative height of difference spectra during annealing; aromatic breathing band at 1600 cm^{-1}. (b) Enthalpy relaxation in PC after Bauwens-Crowet and Bauwens. Annealing temperatures indicated in °C.

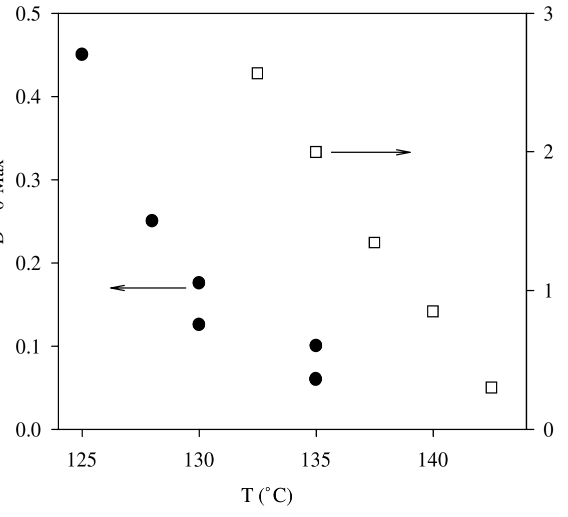

Fig. 4. Left axis, filled circles: steady-state change in population of conformers, from Fig. 3a. Right axis, empty squares: steady-state change in enthalpy, from Fig. 3b.

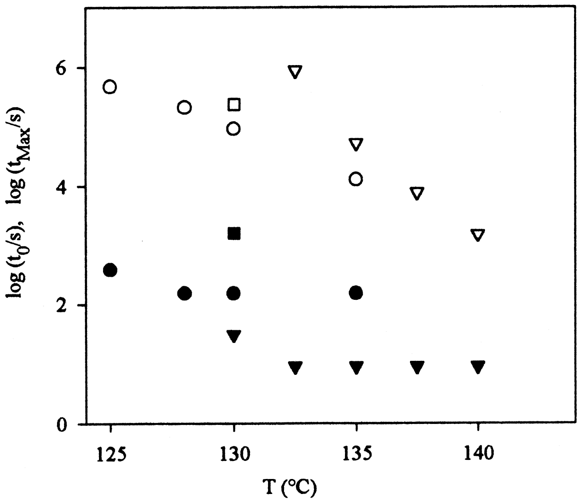

Fig. 5. Timescale of relaxation as defined on Fig. 3. Filled symbols, t_0; empty symbols, t_f. Triangles, DSC; circles, IR; squares, volumetric relaxation.

transition in this work due to the sample transfer method described above to avoid indirect quenching.

The comparison between IR spectroscopy and DSC results can be quantified by making an estimate of the rate of change and of the total change in conformational energy induced by the observed shift from t–c to t–t conformers. The rate of change can be measured by the slope of relative change in amplitude or of enthalpy relaxation, against log time, and by the timescale at start and end of relaxation, defined by the intercepts t_0 and t_f with initial and final level. These intercepts, defined schematically in Fig. 3a and obtained from IR spectroscopy (this work), DSC [3] and volume relaxation [13] are compared in Fig. 5.

When comparing total relaxation amplitudes from IR spectroscopy and DSC, one can either compare amplitudes at a single temperature (i.e. compare saturation levels in Fig. 3) or compare the rate of change of saturation level with temperature (i.e. compare slopes in Fig. 4). The second method is preferable in order to eliminate the effect of the different cooling rates in the two experiments. Assuming equal extinction coefficients for t–t and t–c conformers, the fraction of conformers which have changed conformation is $4 \times \Delta A_D/A_0$. (In fact, this relationship is somewhat insensitive to the ratio of extinction coefficients: if this ratio is 2, the fraction of altered conformers is $4.5 \times \Delta A_0/A_0$.) The change of the steady-state value of this quantity with temperature can be obtained from the slope of Fig. 4 (circles). The corresponding change in conformational energy can be evaluated by multiplying this value by the energy difference between conformers, taking literature values given below. For comparison of rates of change, the slope of curves in Fig. 3a is obtained at each temperature and the corresponding conformational energy relaxation rate is obtained as before. These values are compared with the corresponding values for enthalpy relaxation in Table 1.

Estimates of the difference in energy between t–c and t–t conformations vary in the literature between 0.46 and 2.75 kcal/mol (1.92–11.50 kJ/mol or 7.56–45.3 kJ/kg). Tekely and Turska [7] obtained a difference of 1.82 kcal/mol between t–c and t–t planar conformations of diphenyl carbonate (DPC) taking account of the inherent torsional barrier to rotation and a Lennard-Jones interaction potential between non-bonded atoms, but noted that the lowest energy conformation is non-planar and occurs when the phenyl rings are perpendicular to the carbonate group plane. Hutnik et al. [8] included electrostatic interactions and adjusted bond angles to account for changes in bond lengths and bond angles, and obtained $\Delta E = 1.7$ kcal/mol. By taking polarization of carbon and oxygen atoms into account, Laskowski et al. [9] obtained a somewhat higher value of 2.75 kcal/mol from ab initio self-consistent field calculations and found good agreement between unperturbed dimensions resulting from their model and experimental values, lending support to their result. Schmidt et al. [6] obtained an experimental value of 0.46 kcal/mol from the temperature dependence of the ratio of absorbances for the 1265 and 1223 cm^{-1} components of the C–O–C vibration for solutions of PC in CDCl$_3$, but assumed the discrepancy with calculated values was influenced by intermolecular interactions with the solvent. In a more recent work [10], they found that when electron correlation is included, quantum mechanical calculations lead to a much reduced energy difference between c–t and t–t structures, which in the event of specific polymer–solvent interactions may even result in an increase in c–t content with decreasing temperature.

The limits of the estimate of the change in conformational energy resulting from the present IR spectroscopy

Table 1
Change in conformational energy from IR spectroscopy and enthalpy relaxation from DSC

	IR 1600 cm^{-1} band		DSC
Unit U	$\Delta A_D/A_0$ (%)	Conformational energy (kJ/kg)	Enthalpy (kJ/kg)
Slope 130°C (U/decade)	0.0533	0.0161–0.0966	0.372
Slope 135°C (U/decade)	0.0418	0.0126–0.0757	0.567
Steady state 130°C (U)	0.1483	0.0449–0.0269	3.14 (extrap.)
Steady state 135°C (U)	0.0805	0.0243–0.146	2.0
Slope Fig. 4 (U/K)	0.033	9.98×10^{-3}–0.0598	0.23

measurements are compared with results of DSC measurements in Table 1 for temperatures at which results from both techniques are available. IR spectroscopy measurements clearly yield a much lower estimate than DSC.

3.3. Possible experimental artefacts

The possibility that part of the difference between IR spectroscopy and DSC results arises from experimental artefacts requires examination. Sample heating clearly occurs when the sample is left in the beam: this produces a visible increase in t–c content. Precautions were taken to ensure that this does not affect the experimental results. The effect should remain small (or rather, constant for all measurements) if the sample remains in the beam for the same length of time for all measurements; hence 16 scans were used for all annealing times rather than increasing the number of scans in the hope of increasing signal-to-noise ratio at long times. However, it was noted that the change in the spectra with time in the beam increases with annealing time (i.e. with decreasing distance from equilibrium). Thus it is not impossible that heating in the beam during scanning could lead to an apparent premature saturation and hence to an underestimate of the saturation level. It is highly unlikely that this problem could explain an order of magnitude difference.

As stated above, it was found that use of difference spectra led to far less scatter than other methods, such as curve fitting to obtain peak height and widths. However, the populations of conformers are proportional to the peak areas, not their heights. The method used here only gives the change in peak heights, which were not always easy to measure in cases where the difference spectrum was not of the characteristic wiggle shape shown on Fig. 2. It was noted that the maxima and minima of the difference spectra occurred at 1604 and 1587 cm^{-1} (rather than 1595 cm^{-1}). This could have been the result of interference between changes in population and possible frequency shifts or from the effect of annealing on the intense neighbouring absorption of the aromatic rings at 1505 cm^{-1}. This absorption is not reported in the literature as being sensitive to conformation and it was not possible to check whether annealing produced any changes in this band in the films used in this investigation because of saturation. Because the films were produced by solution casting, surface tension is expected to produce some degree of orientation in the plane of the films. Annealing is likely to relax orientation to some extent. This might affect the 1505 cm^{-1} absorption leading to a change in shape and level of the baseline in the vicinity of the 1600 cm^{-1} doublet investigated here. This could explain the discrepancy between the expected and observed wavenumbers at the maxima of the difference spectra and also the negative baseline frequently observed in the difference spectra, indicating that absorbance of the 1505 cm^{-1} band decreases slightly during annealing. This should not much affect the measured values of ΔA_{D}; however the error due to this effect should also be an underestimate.

Hence, although experimental difficulties lead to an underestimate of the effect of annealing on conformer populations, these difficulties alone cannot explain the order of magnitude difference between measurements of enthalpy relaxation and estimates of changes in conformational energies.

4. Discussion

It is clear from Table 1 that the present estimate of conformational energy relaxation is an order of magnitude or two lower than direct DSC measurements, even when Laskowski et al.'s high value of 2.75 kcal/mol for the energy difference between conformers is used. Possible causes of this discrepancy will now be discussed.

Changes in t–t and t–c populations are not the sole source of enthalpy relaxation; as shown by Jones [11], diffusion of t–c conformers along the chain can occur with no change of populations; this mechanism may contribute to enthalpy relaxation via a modification of interchain interactions, which should not show up in the IR spectra. Interchain interactions may be thought of as of the same nature as frustration energy in spin glasses; this energy depends on the population of pairs of conformers rather than that of individual conformers. Along similar lines of thought, Drozdov [12] has recently developed a model for structural relaxation in disordered systems, specifically glassy polymers, based on the concept of cooperative relaxation by random hopping between traps. He was able to predict the different enthalpy and volume relaxations observed on the same polymer, albeit with a large set of adjustable parameters. Observations of volume relaxation by Washer [13] in this laboratory have indeed shown that volume relaxation is faster than enthalpy relaxation at the same temperature, that it reaches steady state at shorter times (3300 min at 130°C) and that if relaxation is expressed by means of a "structural temperature", the changes in structural temperature are approximately four times larger from enthalpy relaxation than from volume relaxation in the temperature range 110–130°C. It is interesting to note that the same ratio of approximately 4 is obtained between enthalpy relaxation and the largest estimates of conformational energy relaxation. Fig. 5 indicates that the timescale for completion of relaxation follows similar trends for conformational rearrangements, for volume relaxation and for enthalpy relaxation in the immediate vicinity of T_{g}; however, t_{f} for enthalpy relaxation appears to increase much faster with decreasing temperature once temperature decreases below approximately $T_{\mathrm{g}} - 15$ K. The timescale of conformational relaxation at 130°C observed in the present investigation is much closer to that of volume relaxation observed by Washer [13] than to that of enthalpy relaxation observed by Bauwens-Crowet et al. [3]. Similar differences in behaviour between volume and enthalpy relaxation have been observed by Wimberger-Friedl and de Bruin [14] at room temperature, where they observed volume relaxation after ageing for a few months (this corresponds to t_0 as defined here) whereas extrapolation of enthalpy relaxation to room temperature leads to the prediction that t_0 should be on the scale of thousands of years [15].

The present results thus suggest that conformational changes observed during annealing of glassy polymers are closely linked with volume relaxation, but are not directly connected with enthalpy relaxation.

5. Conclusions

The purpose of the present investigation was to check whether enthalpy relaxation could be quantitatively linked to conformational rearrangements, measured by IR spectroscopy; the result is clearly negative. Although qualitatively and phenomenologically similar, there are distinct differences between IR and DSC results, both in terms of the magnitude of relaxation and of its timescale. Conformational rearrangements are faster than enthalpy relaxation, in the sense that steady state is attained after a shorter time, particularly at temperatures below $T_g - 15$ K. It is interesting to note that volumetric relaxation appears to occur on the same timescale as conformational, rather than enthalpy relaxation.

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