A New Model for Structure of Poly (ethylene terephthalate) in its Glassy State

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Synopsis

A new realistic, structural model is proposed for the glassy solid state of poly(ethylene terephthalate) (PET).   The model is considered basing on crystallization behaviors from the glassy state of PET, and in particular including the evidence from the estimation of chain folding energy in this report.   When PET is quenched from its melt into the glassy state, irregular folds with lower conformational energy remain in glassy structure and disturb the three dimensional arrangement of the chains connected with the folds.   In conclusion, we suggested that the structure of glassy PET is not in amorphous state which is represented by the interpenetrating random coil model, but in frozen metastable state which can be approached from the chain folded structure of polymer crystals.

1. INTRODUCTION

Since the beginnings of polymer science, it has been generally accepted that amorphous polymers (crystallizable and noncrystallizable) consist of randomly coiled, entangled chains with no local order.   This model, however, is not what was established from structural evidences. The success of the random coil concept for polymer conformation in explaining the properties of dilute solutions led to adopt conventionally

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this model for the condensed structure of amorphous polymers.   It was
for long only a support for this model that a single molecule in mol-
ten or glassy states had been inferred to possess the same unperturbed
random coil conformation as in a theta solvent from sound thermodynamic
reasoning (1).   Structural investigators, however, could not decide
its validity with direct evidences for the sake of lack of experimen-
tally appropriate techniques, and believed this model from the fact
that amorphous polymers show the same type of diffuse halo on a x-ray
photograph as do simple liquids.

Recently, two experimental developments have occurred.   Electron
microscopes have produced evidence which can be interpreted to mean
that domains of local order exist in the glassy state (2).   On the
other hand, small angle neutron scattering studies on polymer matrices
containing small percentages of their deuterated analogs give evidence
that in the glassy state, polymer chains exhibit their unperturbed
dimension (3).   At the present, each conclusion derived from these
different experimental techniques is not consistent in chain conforma-
tion of glassy solid.   It seems timely, therefore, to describe our
view for structure of amorphous polymers, mainly glassy poly(ethylene
terephthalate) (PET) at the molecular level.

We have been studying crystallization of PET from the glassy state.
In the previous papers (4,5), we suggested that so called " cold
crystallization " may not be attributed to the diffusion of molecules
as a whole but to locally conformational changes of molecules because
of their poor mobility at a temperature slightly higher than T_g.   The
probable conformation changes in this case should be the one from gau-
che to trans accompanied by rotational motion of molecular segments.
This was confirmed with the infrared study of crystallization process.
This crystallization is unique, because such a crystallization occurs
in the transition not from liquid but solid.   From these facts, we
considered that the glassy amorphous state is an intermediate meta-
stable state in which the crystallization is intercepted owing to some
obstacles.   It was assumed by us that this interception of crystalli-
zation is to be caused by the irregular folding of polymer molecules
which disturbs the three dimensional arrangements of chains adjacent
to the folds.   In this paper, we will describe our assumption to be
reasonable from the estimation of chain folding energy, and propose a
new model for the molecular structure of glassy PET approached from
polymer crystals with chain foldings.

2. THE CONFORMATION OF REGULAR FOLDS IN LAMELLAR CRYSTALS

We had already reported that single crystals of PET could be pre-
pared by evaporating the solvent slowly from dilute solution (6).
Electron and x-ray diffraction investigations on these crystals showed
that the molecular axis orients with an inclination of about 35° to the
normal direction of basal plane in lamella. Morphological observation
indicated that the chain foldings occur in the (010) plane alone. The
interesting chain inclination could be interpreted by which the cry-
stallographic (001) plane of the triclinic lattice lies in the basal
plane of the lamellae. It is, therefore, presumed that chain foldings
in crystals which bring the succeeding chain segment into proper regis-
ter with their neighborings, should be unique and highly regular con-
formation not easily accessible to the PET chain.

In this paper we determine the conformation for regular folds from
the following principles: (a) the
conformations of PET chains are
basically determined by the inter-
nal rotation angles, (b) the cry-
stalline part is not deformed where
it is connected with the fold part
($-CO-O-CH_2-CH_2-O-CO-$), and (c) the

TABLE 1 The values of internal rotation barriers

Bonds	U_0 Kcal/bond
$-C-C-$	2.8
$-C-O-$	2.7
$-O-CO-$	0.5

TABLE 2 Van der Waals radius (r_{min}), polarizabilities (α), the effec-
tive number of electron (N) and electrostatic charge (q) of
various atoms, $e_{jk} = (3/2) e (\hbar/m^{1/2}) \alpha_j \alpha_k / ((\alpha_j/N_j)^{1/2} + (\alpha_k/N_k)^{1/2})$
and $d_{jk} = e_{jk} r_{min}^6 /2$

Atoms	r_{min}(A)	$\alpha \times 10^{24} cm^3$	N	q in unit of e
C	1.70	0.93	5.2	-0.061
H	1.20	0.42	0.9	0.078
O_{ether}	1.52	0.64	7.2	-0.202
$O_{carbonyl}$	1.52	0.84	7.4	-0.423
$C_{carbonyl}$	1.70	1.30	4.7	0.610
$C_{aromatic}$	1.85	0.93	5.5	0.0
$H_{aromatic}$	1.20	0.42	0.9	0.0

conformation of folds is determined as the minimum of conformational
energy. The energy calculations were made according to the method
reported by Scheraga et al. (7). The energy function is as follows;

$$E = \sum_i U_0(1 + \cos 3\tau_i)/2 + \sum_{j>k} (d_{jk}/r_{jk}^{12} - e_{jk}/r_{jk}^6) + \sum_{j>k} q_jq_k/Dr_{jk}$$

where τ_i is the bond rotational angle of i-th bond, r_{jk} is the distance between nonbonding atom j and k and the other parameters are evaluated from the values of Table 1 and Table 2. The effective dielectric constant D is taken to be 2 in all cases. The values of molecular and crystal parameters that are used for the calculation of fold conformation are based on the atomic ooordinates determined from x-ray pattern (8).

The most probable conformation of the regular fold derived from above calculations is shown in Figure 1 (a) and (b). The energy of this fold, assuming the orystal-line conformation as reference state, is

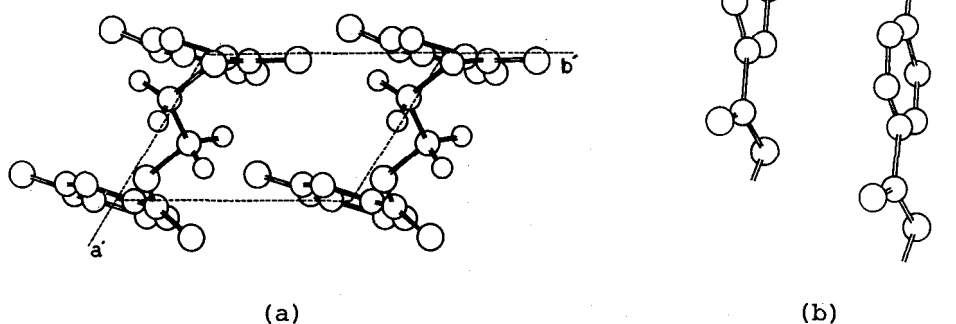(a)   (b)

FIGURE 1 The conformation of the regular fold in crystals.
         (a) is the top view and (b) is the side view.

5.0 kcal/mol. This energy value is high in comparison with those of other possible conformations. It, therefore, can be suggested that the regular fold in lamellar crystals is formed when the chain stems connected with the folds become stable crystalline state with lower energy.

3. THE CONFORMATIONAL ENERGY OF IRREGULAR FOLDS

In the previous section, it was shown that the conformational energy of the regular fold in lamellar crystals is considerably high. To confirm the possibility of chain folds with lower energy, the energy of folds free from the crystallographic requirements was calculated here. The principles of its calculation are as follows: (a) the folds are formed with a part of the PET chain, $-CO-O-CH_2-CH_2-O-CO-$, (b) the parallel chains connected with the fold part are allowed to displace

·relatively in a chain direction and to
change their distance and setting angle.
From the above calculations, we can find
a number of irregularly folded conforma-
tion with the lower energy than the regu-
lar one.   Figure 2 shows an example of
such irregular folds.   The value of the
lowest energy among the irregular folds
is -1.1 kcal/mol. assuming the crystalline
conformation as reference state.

4. DISCUSSION AND CONCLUSIONS

It is strongly supported from the
evaluation of fold energy that the struc-
ture of glassy PET is an intercepted one
in the course of crystallization as sug-

FIGURE 2 An example of
        irregular folds.

gested in our previous papers (4,5).   When PET is quenched from its
melt into the glassy state, irregular folds remain in the glassy
structure and disturb the three dimensional arrangements of the chains
adjacent to the folds.   It should be noticed that the occurrence of
such situation as mentioned above is most likely due to the well known
inflexibility of the aromatic ring with its attached -COO- groups and
the length of the crystallographic identity period in PET chains.

Furthermore, it can be suggested
that the intramolecular high pack-
ing energy of chain stems caused by
irregular foldings is relaxed with
the local kink conformation of the
intramolecular low energy.   The
real kink conformation, TTGT$\overline{\text{G}}$,
existing in ethylene glycol part
has been confirmed from the infra-
red study on glassy PET by us (5).

In conclusion, when one con-
siders models of the molecular con-
formation in glassy PET, intuitive-
ly it seems obvious that neighbor-
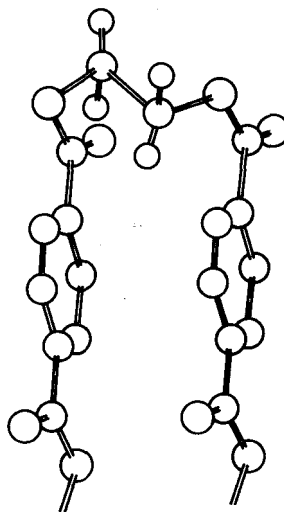ing molecular segments will tend to
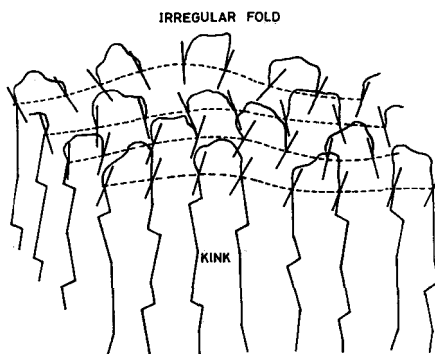be aligned, particularly when one

FIGURE 3 A new model proposed
        for structure of PET in
        the glassy state.

considers the relative density of PET in the amorphous and crystalline
state (9).   Although intuition is obviously not sufficient, the evi-
dence of fold energy discussed above tends to substantiate this intui-
tion.   In other words, one can suggest that the structure of PET
should not be in "amorphous" state which is represented by the inter-
penetrating random coil model, but in "frozen" metastable state which
can be approached from the chain folded structure of polymer crystals.
And the cold crystallization behaviors, as pointed out the beginning
of this article, can be interpreted as the re-conformation of chain
folds to the regular ones resulting the proper register between neigh-
boring chains by the translational migration with the conversion of
the distorted gauche to trans.   We also have confirmed that x-ray
diffuse halo of the glassy PET can be explained with intensities scat-
tered by the paracrystals which have largely distorted lattice (10).
Our new model for structure of PET in the glassy state is illustrated
in Figure 3.   In this paper, we have aimed to represent our basical
view points for structure of amorphous polymers, mainly PET.   We will
report elsewhere the experimentally detailed verification for our view.

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