Some applications of photoluminescence for probing polymer relaxation processes

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Acknowledgments
Polymer motions, phase transitions and polymer relaxation processes

Which is the correlation between morphology

Phase transitions and relaxations processes
- Polymer systems and morphology
- Polymer motions, phase transitions and polymer relaxation processes
- Photoluminescence spectroscopy and polymer relaxation processes
  - Fluorescence
  - Phosphorescence
  - Quenching processes
  - Time resolved spectroscopy
- Luminescence in polymers
  - Non-fluorescent polymers (host-guest systems)
  - Polymers modified with luminescent groups
  - Intrinsically luminescent polymers
  - Conjugated luminescent polymers
  - Electroluminescence and photoluminescence
Polymer systems

- Macromolecules = several chemically bonded repeated units
- Polymer matrix = several macromolecules organized according a certain morphology
- Special properties resulted from the macromolecular structure and from the morphology
Polymer systems: morphology of semicrystalline polymers

The Reentry Problem in Lamellae

MODEL OF LINEAR POLYETHYLENE

L. H. Sperling, Introduction to Physical Polymer Science, 1986
Polymer systems: amorphous polymers

From Little Molecules to Big Molecules

(a)  (b)
Polymer systems: crosslinked polymers
First order phase transitions = thermodynamic process

\[ G^\alpha = G^\gamma \]

\[
\left[ \frac{\partial (G/T)}{\partial (1/T)} \right]_p = H \quad \left[ \frac{\partial G}{\partial T} \right]_p = -S \quad \left[ \frac{\partial G}{\partial P} \right]_T = V
\]

\[ \alpha = \frac{1}{V} \left[ \frac{\partial V}{\partial T} \right]_p - \frac{1}{V} \left( \frac{\partial^2 G}{\partial P \partial T} \right) - T \left[ \frac{\partial^2 G}{\partial T^2} \right]_p - \left[ \frac{\partial H}{\partial T} \right]_p = C_p \]

\[
\left[ \frac{\partial^2 G}{\partial P^2} \right]_T = \left[ \frac{\partial V}{\partial P} \right]_T = -\kappa_T V
\]
Evidences of first order phase transition in crystals: melting point

Typical example of melting point
First order phase transition in a semicrystalline polymer (low density polyethylene)

Talhavini, et al. Polymer 1996

Technique: differential scanning calorimetry
Evidences of crystal structure in semicrystalline polymers: X-ray diffraction (low density polyethylene)

Talhavini, et al. Polymer 1996
Polymer relaxation processes: glass transition temperature in an amorphous polymer

Technique: differential scanning calorimetry
glass transition temperature in an amorphous polymer by several thermal methods

Differential scanning calorimetry (DSC)

Dynamic mechanical thermal analysis (DMTA)

Atvars, Quimica Nova, 2002
Fig. 1. DSC heating thermograms of: (1) LDPE, (2) EVA-9, (3) EVA-18, (4) EVA-25, (5) EVA-33, (6) EVA-40 and (7) PVAc. Second heating scan. Heating rate 20 °C/min.
Polymer motions, phase transitions and polymer relaxation processes

Effect of the thermal transitions on the molar volume

(a) Translational movements
(b) Rotational movement of large groups
(c) Rotational movements of small groups
Other examples of possible movements in polymers = polymer relaxation processes

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Transitions</th>
<th>Suggested Mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>433°K (160°C)</td>
<td>$T_{1,1}$</td>
<td>Liquid$_1$ → liquid$_2$</td>
</tr>
<tr>
<td>373°K (100°C)</td>
<td>$T_g$</td>
<td>Long-range chain motions</td>
</tr>
<tr>
<td>325 ± 4°K (~ 50°C)</td>
<td>$\beta$</td>
<td>Torsional vibrations of phenyl groups</td>
</tr>
<tr>
<td>130°K</td>
<td>$\gamma$</td>
<td>Motions due to four carbon backbone moieties</td>
</tr>
<tr>
<td>38–48°K</td>
<td>$\delta$</td>
<td>Oscillation or wagging of phenyl groups</td>
</tr>
</tbody>
</table>

Examples of possible movements in polymers chain: poly(methyl methacrylate)

Christoff, Atvars, Macromolecules, 1999
how to access the relaxation processes?

Several techniques: DSC, DMTA, RMN, fluorescence pectroscopy,
De Deus, et al. Macromolecules, 2005 etc
Photoluminescence spectroscopy and polymer relaxation processes

Some examples of methods

- fluorescence
- phosphorescence
- quenching processes
- time resolved spectroscopy
- anisotropy
- etc
Example of steady state fluorescence versus temperature

\[ q_{FM} = \frac{k_{FM}}{k_{FM} + k_{IM} + k_{ST} + k_{DM} [AN]} \]

\[ \ln \left[ \frac{I_F^0}{I_F} - 1 \right] = A - \frac{E_a}{RT} \]
Example: anthracene in low density polyethylene

Talhavini et al., Polymer 1996
Example of steady state phosphorescence versus temperature

\[ \phi_{Ph} = \phi_{ST} \left[ k_{Ph} / (k_{Ph} + k_{nr}) \right] \]

\[ 1 / I_P - 1 / I_0 = B \exp \left( -E_a / RT \right) \]
Phosphorecence of flavones in acrylates and polystyrene

In PS

Christoff, Atvars, Macromolecules, 1999
Phosphorescence in acrylates and polystyrene

Figure 2. A. Temperature dependence of the normalized phosphorescence intensity of probes in PS films. Arrhenius plots for $I_p / I_0$ vs. $1/T$: B. X: (*), and B: (□); C. F0 (○), and F7 (□). $I_0$ was taken as 15 K.

Figure 3. A. Temperature dependence of the normalized phosphorescence intensity of probes in PMMA films. Arrhenius plots for $I_p / I_0$ vs. $1/T$: B. X: (*), and B: (□); C. F0 (○), and F7 (□). $I_0$ was taken as 15 K.

Christoff, Atvars, Macromolecules, 1999
**Activation energies for relaxation processes by phosphorescence emission**

Table 3. Transition temperatures \( T \) \( (K) \) and apparent activation energies \( \text{Ea} \) \( (\text{kJ.Mol}^{-1}) \) for probes sorbed in PS films.

<table>
<thead>
<tr>
<th>Relaxation</th>
<th>( T ) (K)</th>
<th>( \text{Ea} ) (kJ.Mol(^{-1}))</th>
<th>X</th>
<th>Bp</th>
<th>F0</th>
<th>F7</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma' )-relaxation</td>
<td>100</td>
<td>7</td>
<td>108</td>
<td>4</td>
<td>112</td>
<td>2</td>
</tr>
<tr>
<td>( \gamma )-relaxation</td>
<td>144</td>
<td>20</td>
<td>179</td>
<td>12</td>
<td>183</td>
<td>9</td>
</tr>
<tr>
<td>( \beta )-relaxation</td>
<td>197</td>
<td>52</td>
<td>317</td>
<td>43</td>
<td>291</td>
<td>76</td>
</tr>
</tbody>
</table>

\( \text{error} \pm 5\%; \text{b)} \text{error} \pm 10\% \)

Christoff, Atvars, Macromolecules, 1999
Steady state phosphorescence emission versus temperature – several examples

### MASS DIFFUSION IN SOLID POLYMERS

#### TABLE 1. Transition temperatures ($T_{\text{trans}}(\text{K})$) and activation energies ($E_a(\text{kcal/mol})$), from Arrhenius plots of polymer phosphorescence intensity

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$T_{\text{trans}}(\text{K})$</th>
<th>$E_a(\text{kcal/mol})$</th>
<th>Chain segment rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>178</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>PS-PVK</td>
<td>182</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>PS-PIP</td>
<td>183</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>PS-MVK</td>
<td>175</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>PS-MIP</td>
<td>183</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>PS-5-hexen-2-one</td>
<td>175</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>PS-NMA</td>
<td>120</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>PE</td>
<td>163</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>PE-CO</td>
<td>163</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>PE-MVK</td>
<td>163</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>PE-MIP</td>
<td>163</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>~155</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>PMMA-MVK</td>
<td>148</td>
<td>4.2</td>
<td>248 7.6</td>
</tr>
<tr>
<td>PMMA-NMA</td>
<td>189</td>
<td>5.6</td>
<td>245 9.2</td>
</tr>
<tr>
<td>PMMA-NMA-MVK (80:10:10)</td>
<td>173 3.0</td>
<td></td>
<td>236 6.0</td>
</tr>
<tr>
<td>PVC (comm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC (lab)</td>
<td>180</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>PVC-MVK</td>
<td>163</td>
<td>4.7</td>
<td>188 5.0</td>
</tr>
<tr>
<td>PVC-MIP</td>
<td>163</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td>~ 216</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>PAN-PVK</td>
<td>235</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>PAN-MVK</td>
<td>125</td>
<td>2.1</td>
<td>216 9.8</td>
</tr>
<tr>
<td>PAN-MA-MVK (75:20:5)</td>
<td>136 3.7</td>
<td></td>
<td>238 5.8</td>
</tr>
<tr>
<td>PMAN</td>
<td>234</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>PMAN-MVK</td>
<td>238</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>PMAN-MMA-MVK (75:20:5)</td>
<td>230 5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMVK</td>
<td>145</td>
<td>5.8</td>
<td>230 12.2</td>
</tr>
<tr>
<td>PMIP</td>
<td>233</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>PPVK</td>
<td>196</td>
<td>5.7</td>
<td></td>
</tr>
</tbody>
</table>
Using quenching processes of phosphorescence: diffusion of oxygen in polymers

Using excimer emission – example: diphan in polybutadiene

Using excimer emission – example: 1,3-dipyrenyl propane in low density polyethylene

1,3-dipyrenyl propane in LDPE

Table 2. Relaxation temperatures and apparent activation energies, $E_a$ for 1Py(3)1Py in LDPE.

<table>
<thead>
<tr>
<th></th>
<th>unstretched LDPE</th>
<th></th>
<th></th>
<th>Stretched LDPE</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>first heating</td>
<td>cooling</td>
<td>first heating</td>
<td>cooling</td>
<td>second heating</td>
</tr>
<tr>
<td>$T_p$ / K</td>
<td>268</td>
<td>284</td>
<td>*</td>
<td>268</td>
<td>*</td>
</tr>
<tr>
<td>$E_a$ / kJ mol$^{-1}$</td>
<td>11</td>
<td>13</td>
<td>10</td>
<td>6.5</td>
<td>10</td>
</tr>
<tr>
<td>$T_\alpha$ / K</td>
<td>295</td>
<td>300</td>
<td>320</td>
<td>295</td>
<td>300</td>
</tr>
<tr>
<td>$E_a$ / kJ mol$^{-1}$</td>
<td>47</td>
<td>54</td>
<td>77</td>
<td>52</td>
<td>51</td>
</tr>
<tr>
<td>$T_m$ / K</td>
<td>378</td>
<td>366</td>
<td>366</td>
<td>372</td>
<td>377</td>
</tr>
<tr>
<td>$E_a$ / kJ mol$^{-1}$</td>
<td>17</td>
<td>22</td>
<td>**</td>
<td>14</td>
<td>**</td>
</tr>
</tbody>
</table>

* out of the temperature range; ** non-Arrhenius process.
Dynamic of the relaxation

Figure 1. Initial structures of Py3MPy (top) and of LDPE (bottom).

Figure 9. Illustration of an excimer conformation of Py3MPy adsorbed into the LDPE matrix.
Figure 7. Variation of $\ln\left[\frac{P_e}{1-P_e}\right]$ vs. $T^{-1}$ for Py3MPy adsorbed into the LDPE matrix.

Figure 8. Excimer fluorescence intensity of Py3MPy in the LDPE matrix (adapted from ref.\cite{ref}).

Time resolved spectroscopy – example: Diphant in poly(butadiene) and copolymers with styrene

Using time resolved spectroscopy:

Malachite green in polybutadiene

FIG. 1. Molecular structure of malachite green

FIG. 2. Fluorescence decay curves of MG doped in PB measured by using the two experimental systems described in the text. Dots are the experimentally obtained data, and solid lines are fitting curves. (a) In the higher-temperature region biexponential decay is found. (b) In the lower-temperature region the decay curves are well fitted to single-exponential functions.

FIG. 5. Temperature dependence of the fluorescence lifetime of MG in PB.
\[ \tau_{\text{sur}} = \tau_{H}^{0} \left[ \frac{T_{c}}{(T-T_{c})} \right]^\gamma \quad \text{for } T > T_{c}, \]
\[ \tau_{\text{sur}} = \tau_{M}^{0} \exp \left[ \frac{B}{(T-T_{0})} \right] \quad \text{for } T_{c} > T > T_{g}, \]
\[ \tau_{\text{sur}} = \tau_{L}^{0} \exp \left[ \frac{E_{a}}{k_{B}T} \right] \quad \text{for } T < T_{g}. \]
Some remarks

- Several methods can be employed to determine polymer transitions and relaxation processes.
- Photophysical methods are useful in understanding the molecular mechanism of these processes.
- Methods of simulation can be useful to understand the dynamics of these processes – depends on how good is the description of the macromolecular structure.
- There is no general model to correlate the relaxation behavior from photophysical methods and rheological behavior.
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    - phosphorescence
    - quenching processes
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