Some applications of photoluminescence for probing polymer relaxation processes

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Slide 1

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FAPESP

Polymer motions, phase transitions and polymer relaxation processes

Which is the correlation between morphology

⇕

Phase transitions and relaxations processes

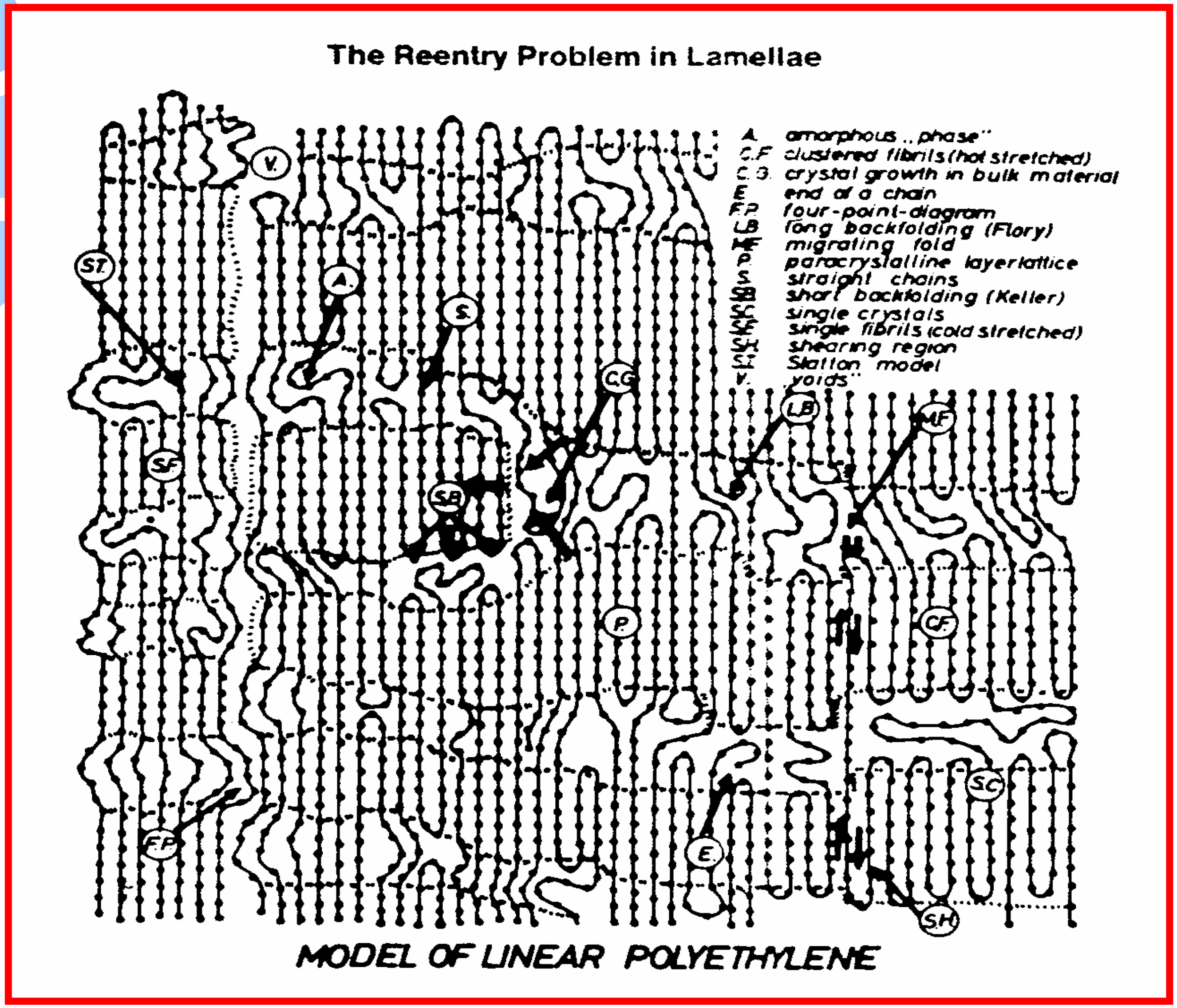
outline

- ☐ 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

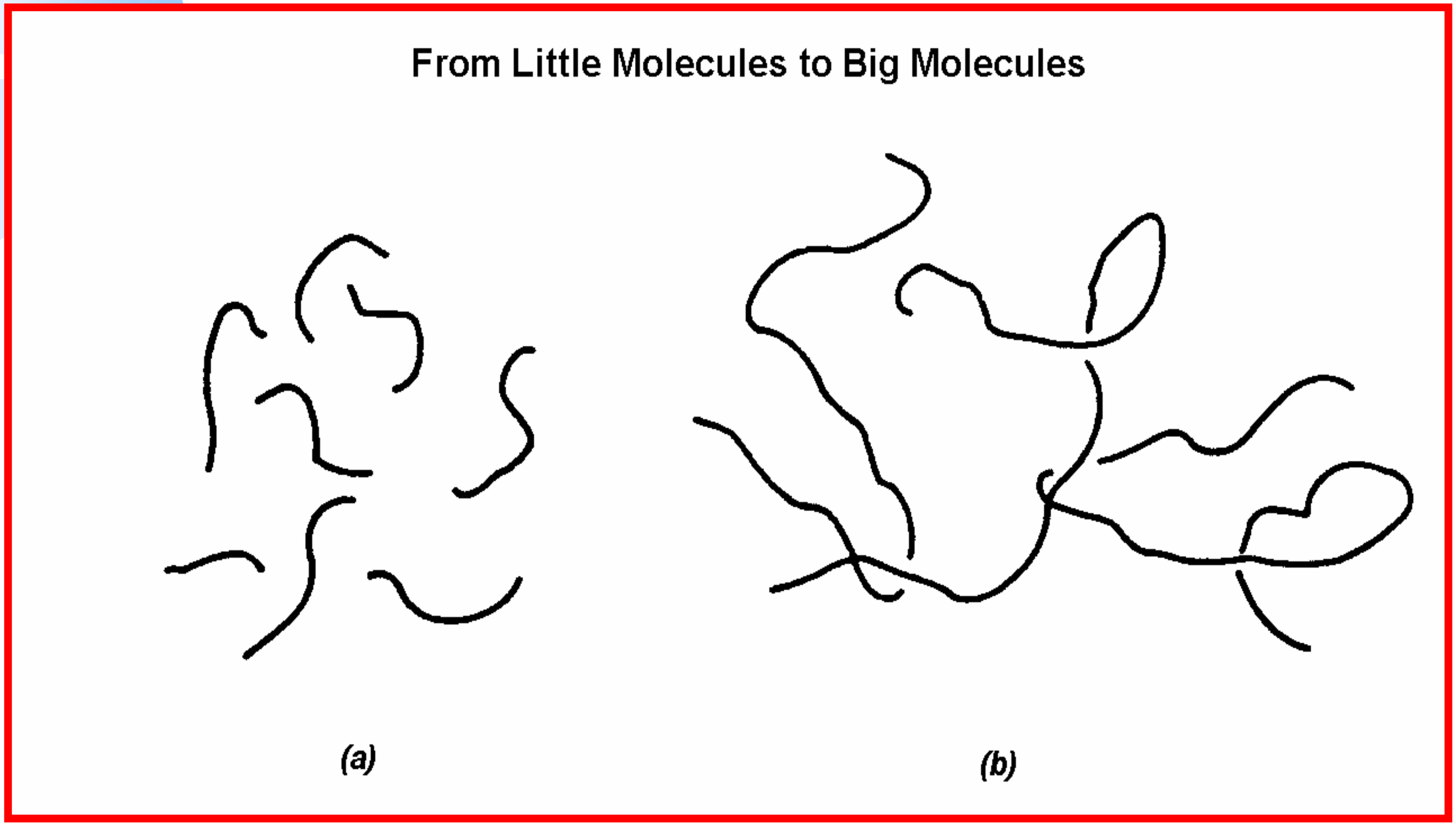
Polymer systems : morphology of semicrystalline polymers


The Reentry Problem in Lamellae

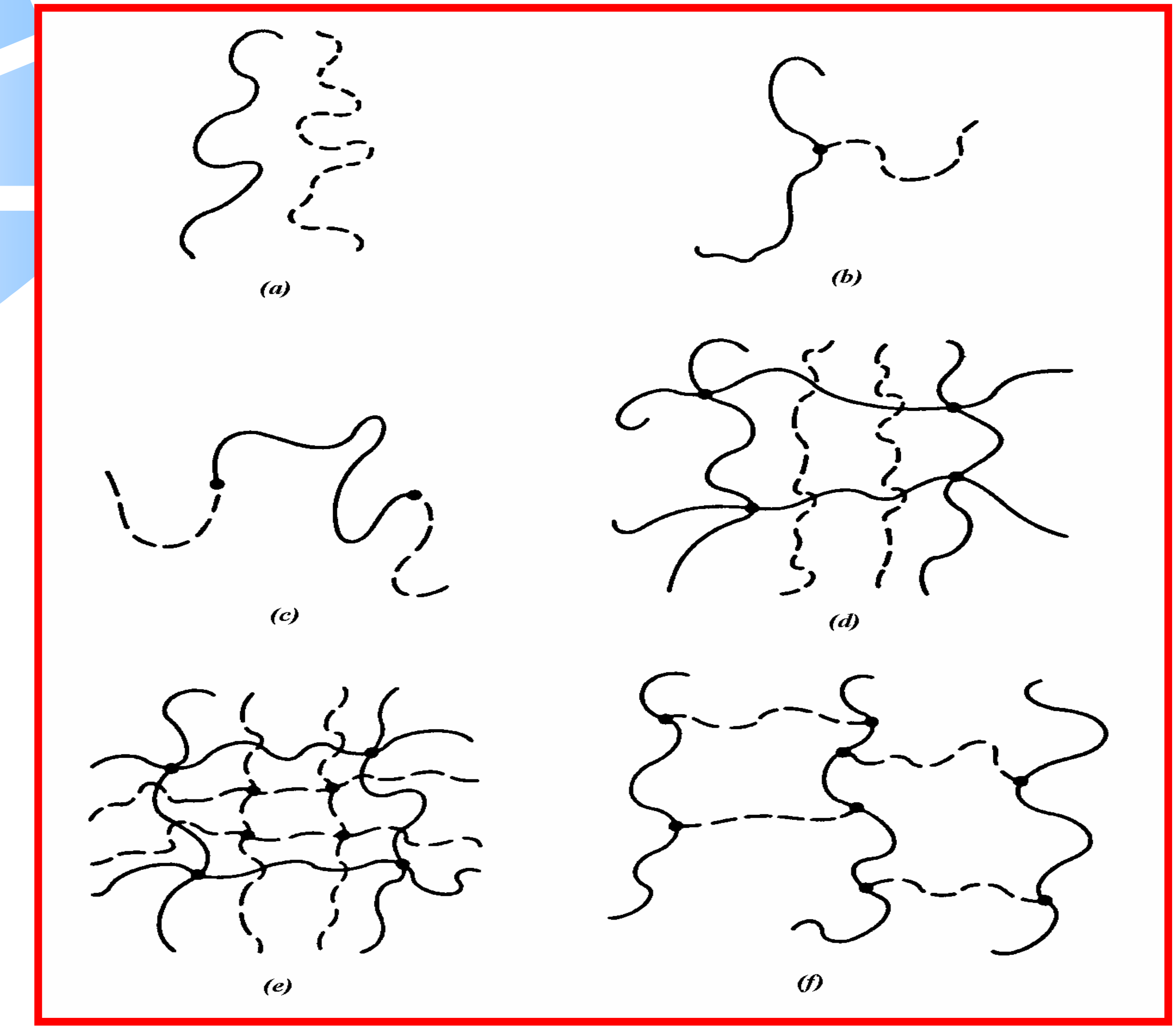
MODEL OF LINEAR POLYETHYLENE

L. H. Sperling, Introduction to Physical Polymer Science, 1986

Polymer systems : amorphous polymers


From Little Molecules to Big Molecules

Polymer systems : crosslinked polymers



First order phase transitions = thermodymanic process

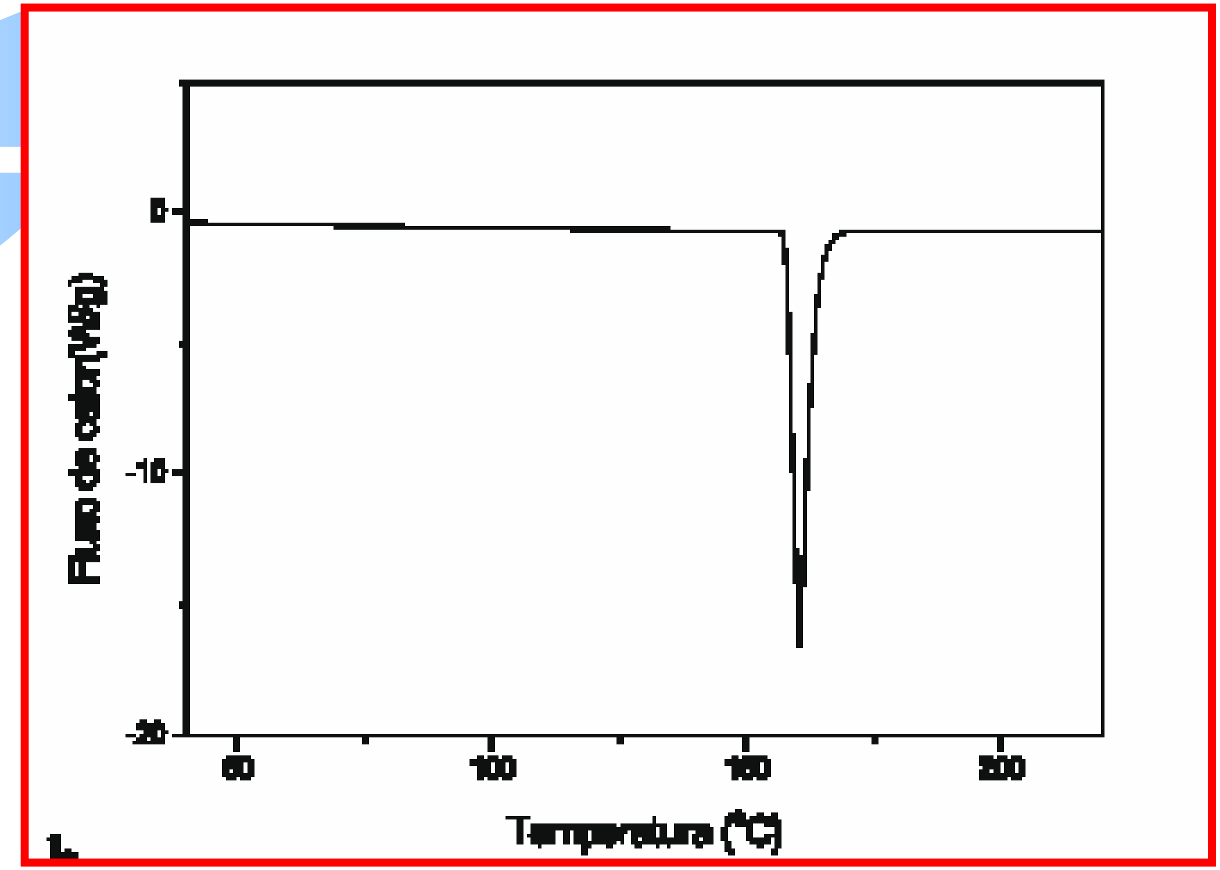
$$G^{\alpha} = G^{\gamma}$$

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

$$\alpha = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P = \frac{1}{V}\left(\frac{\partial^2 G}{\partial P\,\partial T}\right) \qquad -T\left[\frac{\partial^2 G}{\partial T^2}\right]_P = \left[\frac{\partial H}{\partial T}\right]_P = C_P$$

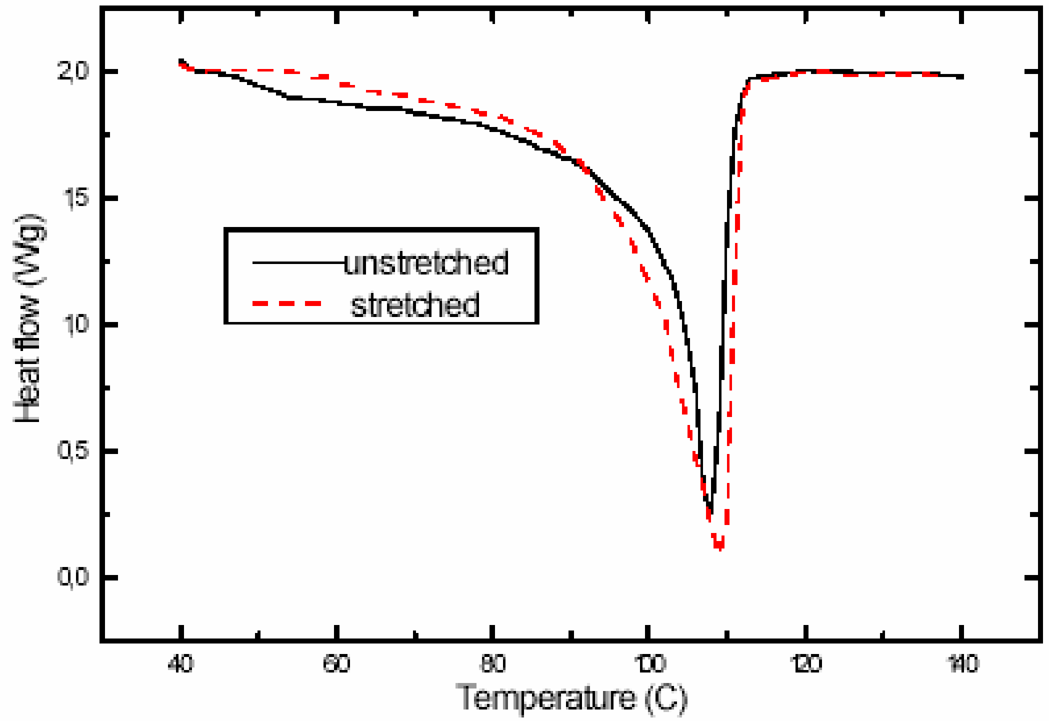
$$\left[\frac{\partial^2 G}{\partial P^2}\right]_T = \left[\frac{\partial V}{\partial P}\right]_T = -\kappa_T V$$

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 polyethyelene)

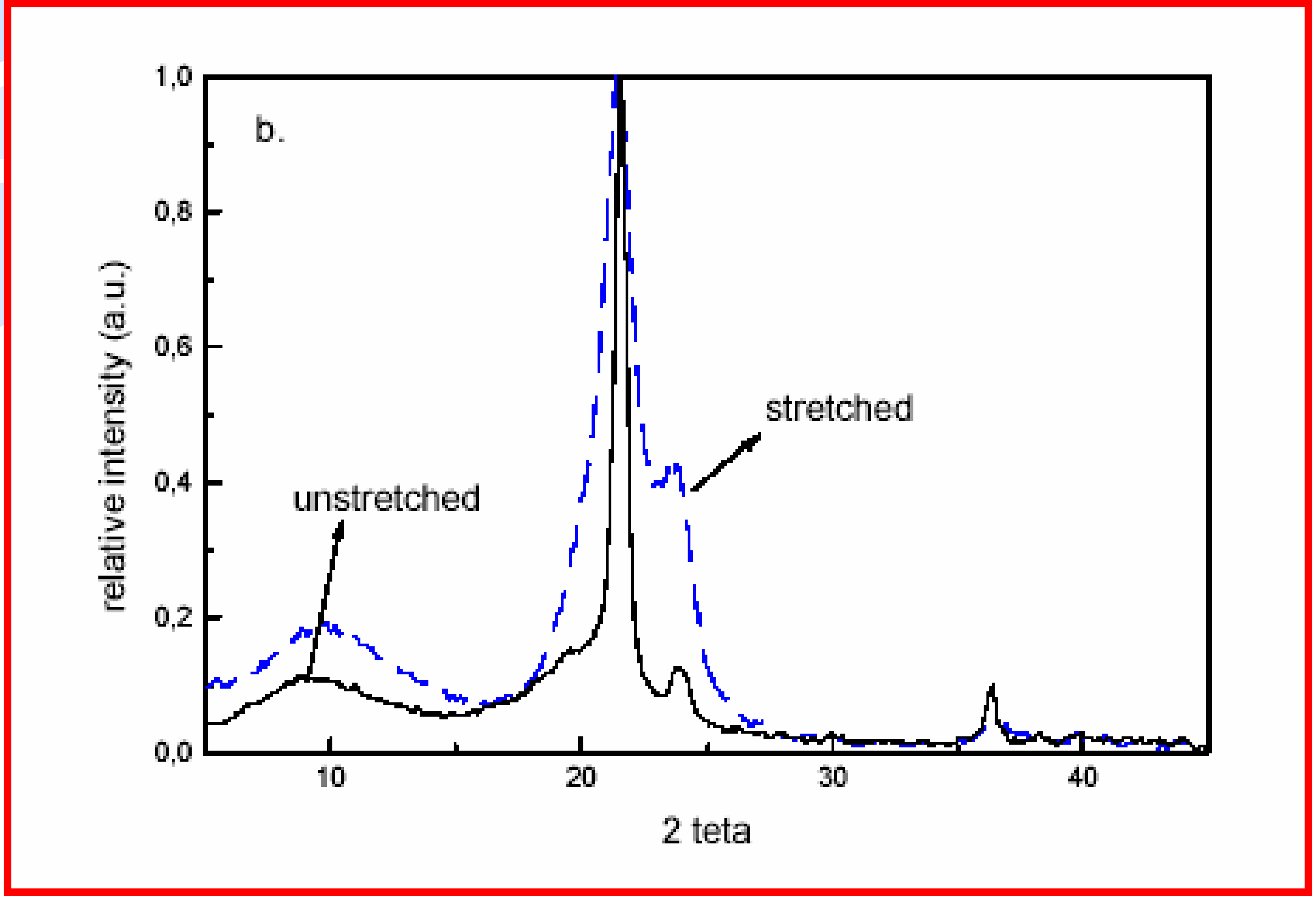


Broad transition

Talhavini, et al. Polymer 1996

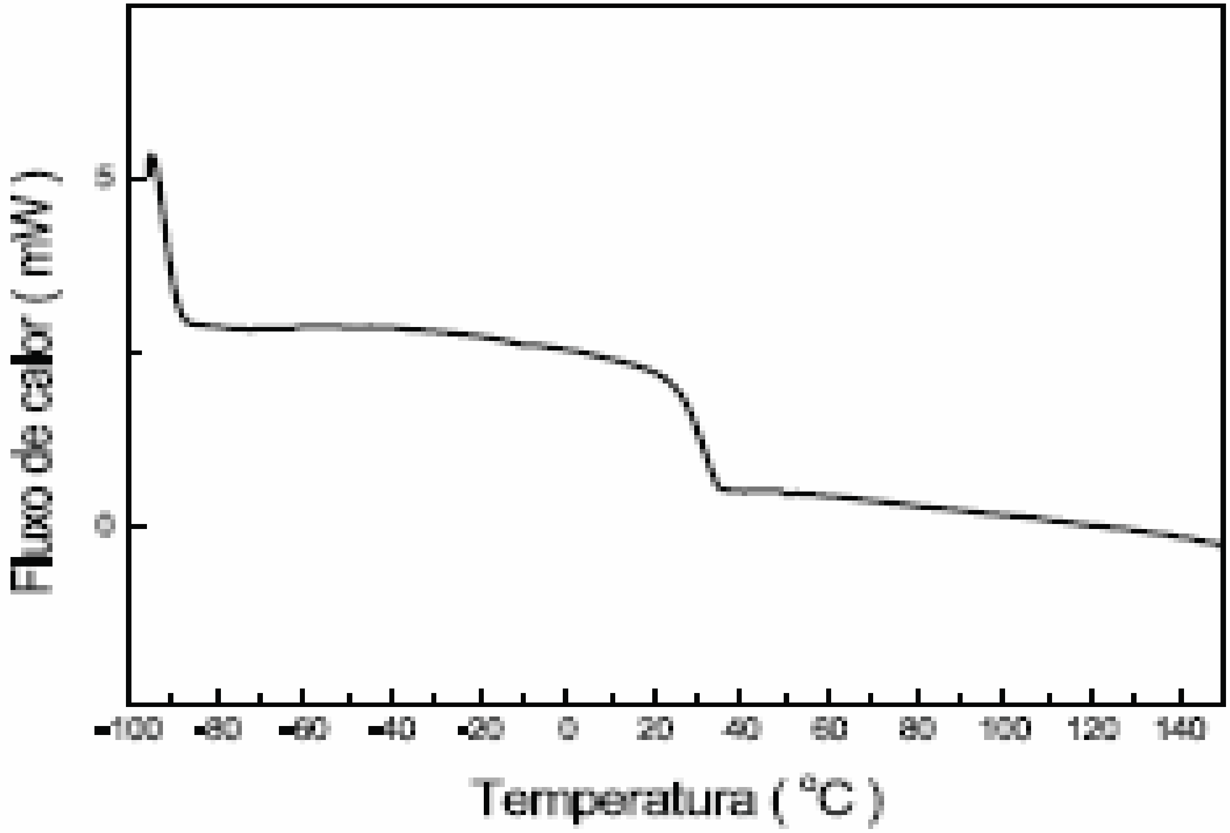
Technique: differential scanning calorimetry

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



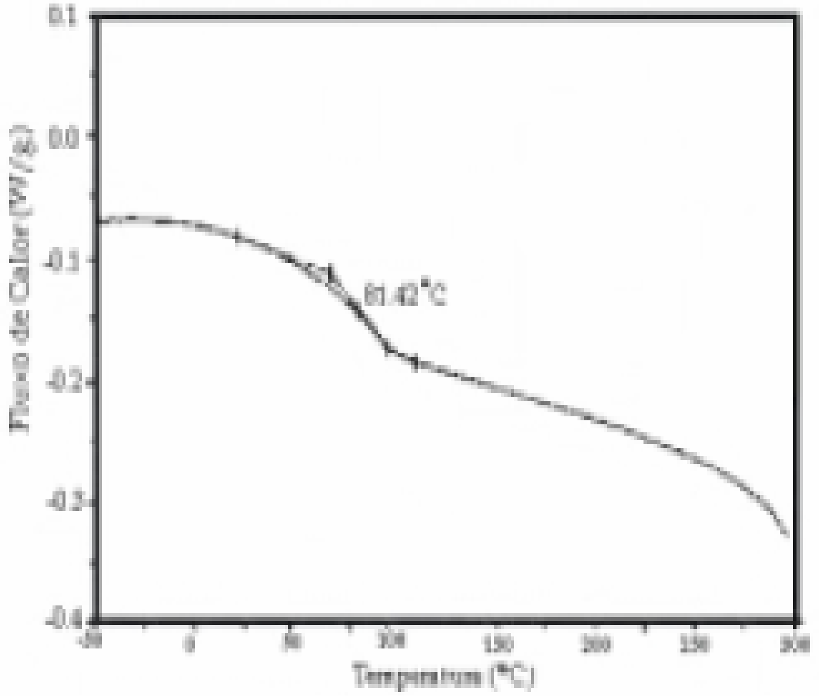
Talhavini, et al. Polymer 1996

Polymer relaxation processes: glass transition temperature in an amorphous polymer

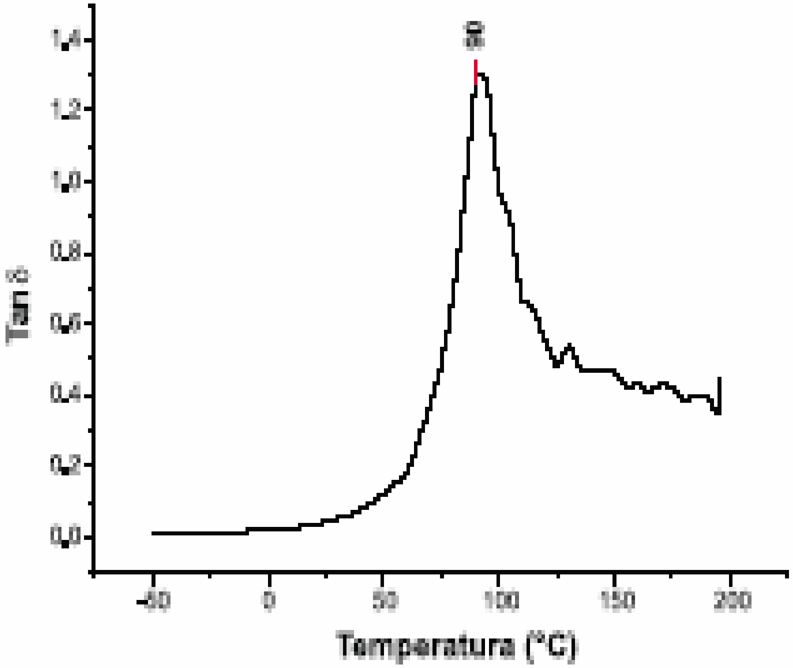


Technique: differential scanning calorimetry

glass transition temperature in an amorphous polymer by several thermal methods



Differential scanning calorimety (DSC)



Dynamic mechanical thermal analysis (DMTA)

Atvars, Quimica Nova, 2002

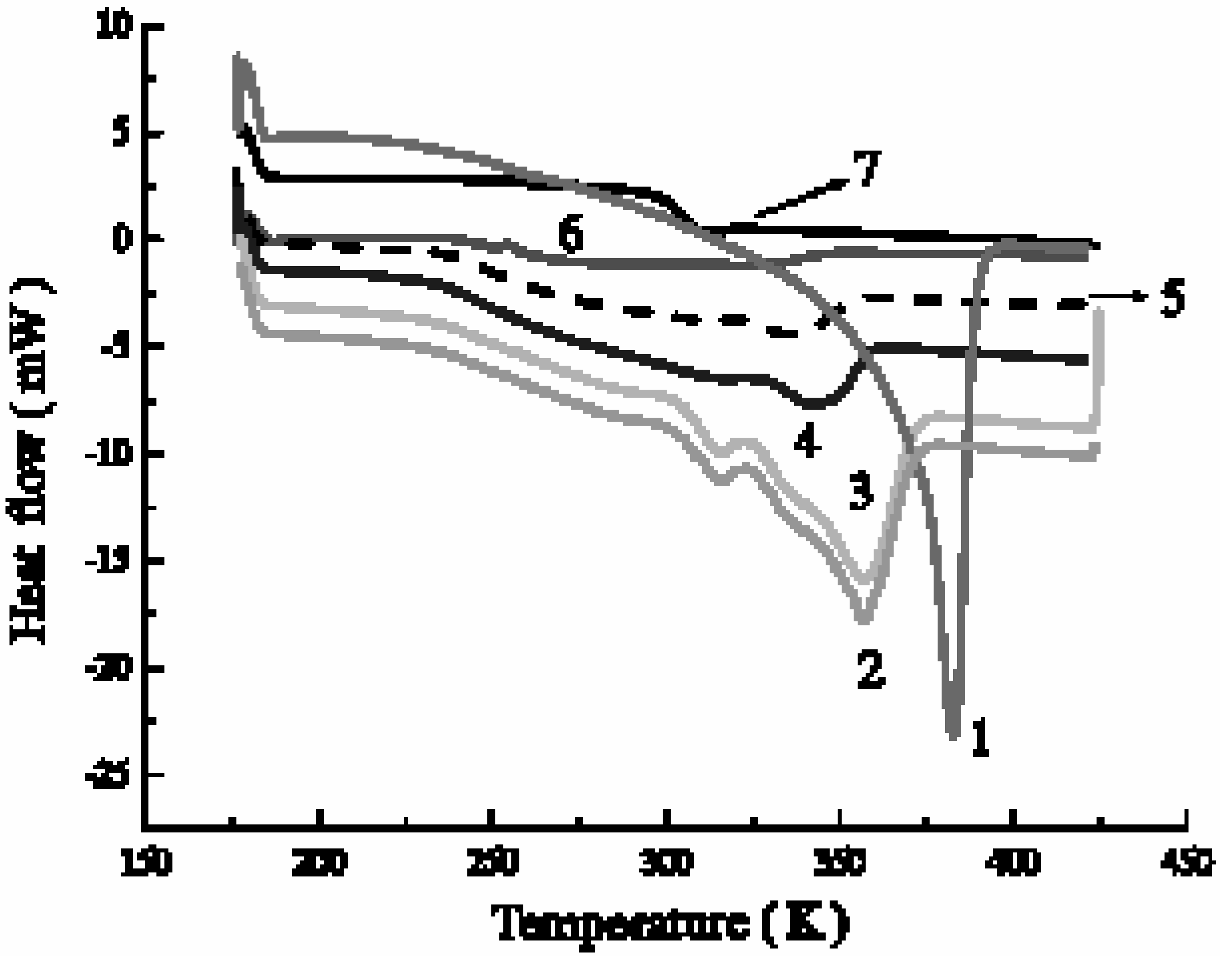
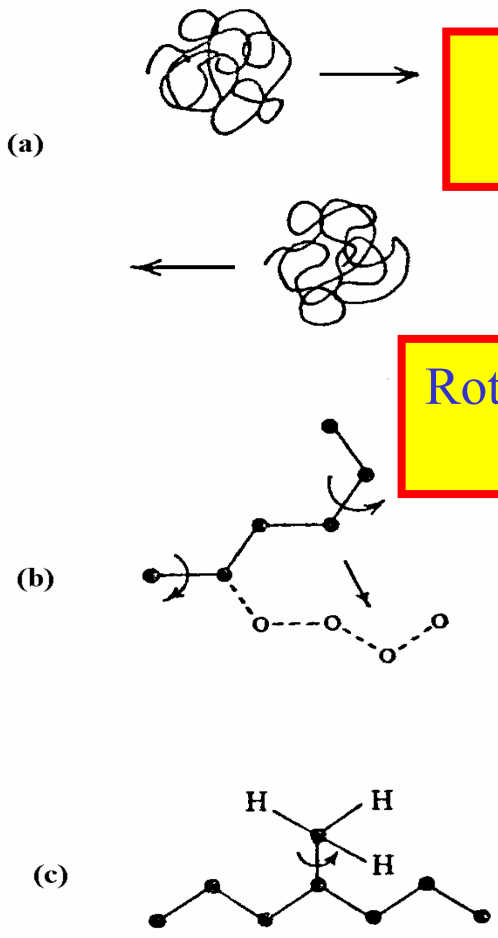


Fig. 1. DSC heating thermograms of: (1) LDPE, (2) EVA-9, (3) EVA-18, (4) EVA-25, (5) EVA-33, (6) EVA-40 and (7) PVAc. Second heating scan. Heating rate 20 °C/min.

Yamaki, et al. Eur. Polym. J. 2002

Polymer motions, phase transitions and polymer relaxation processes

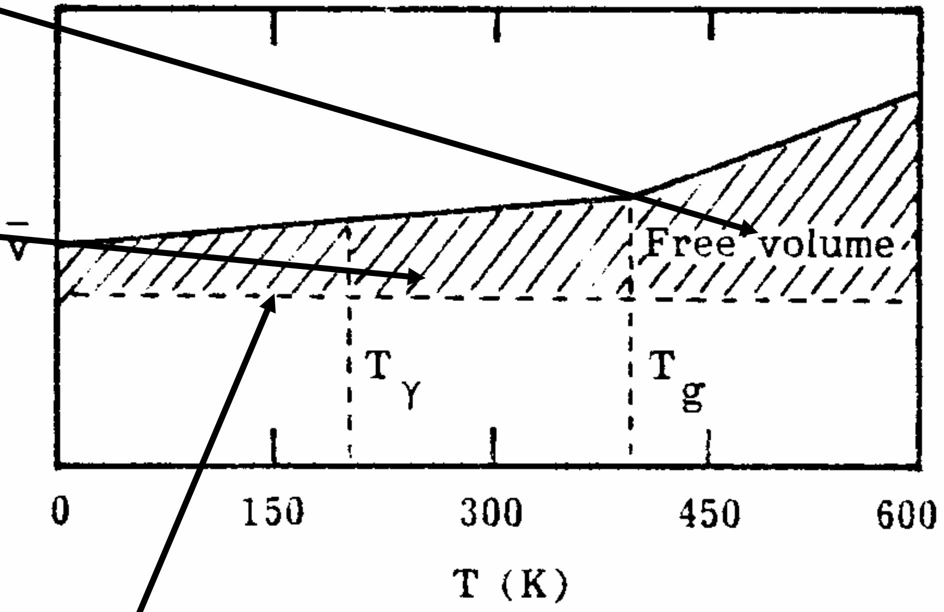
Effect of the thermal transitions on the molar volume



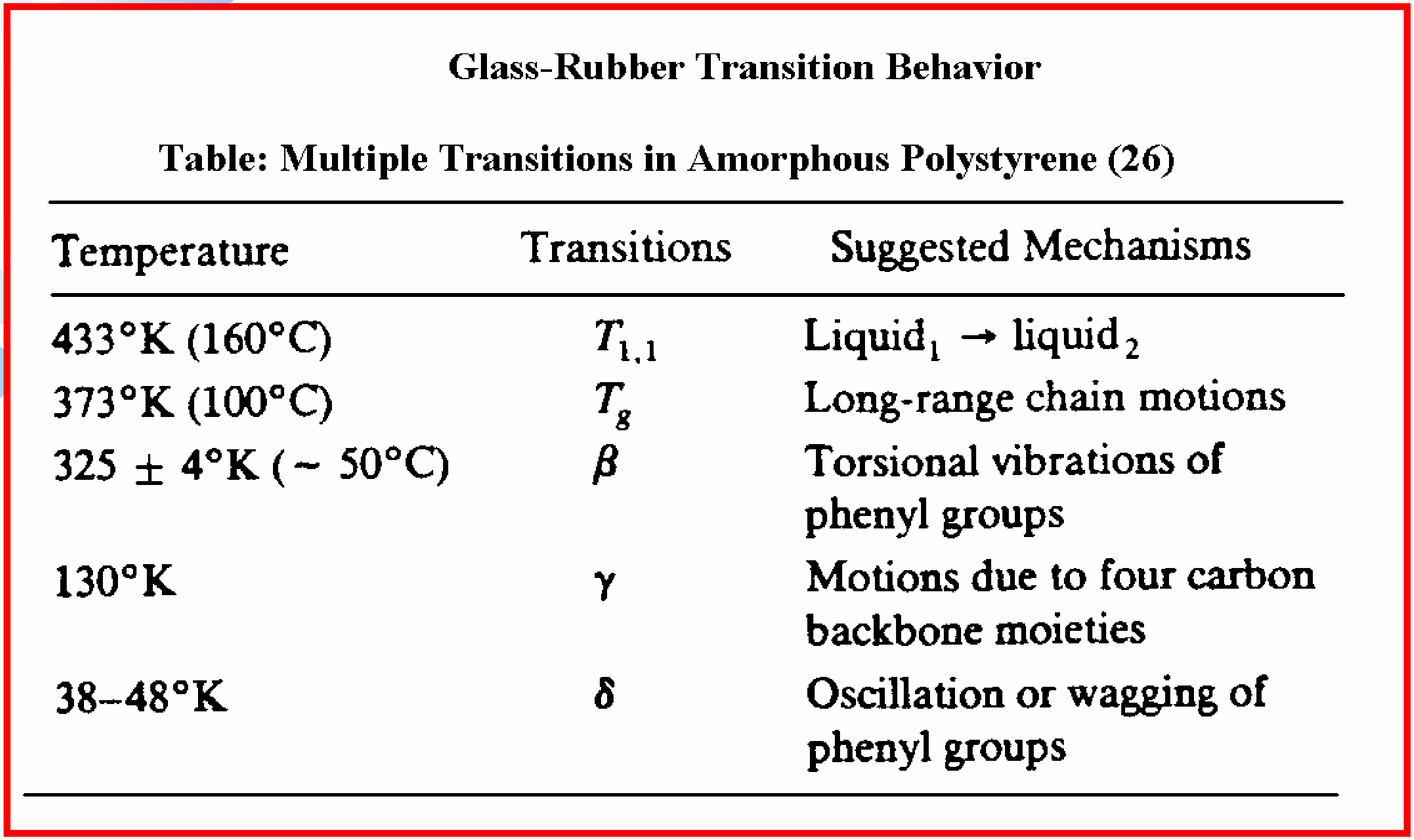
Translational movements

Rotational movement of large groups

Rotational movements of small groups



Other examples of possible movements in polymers = polymer relaxation processes



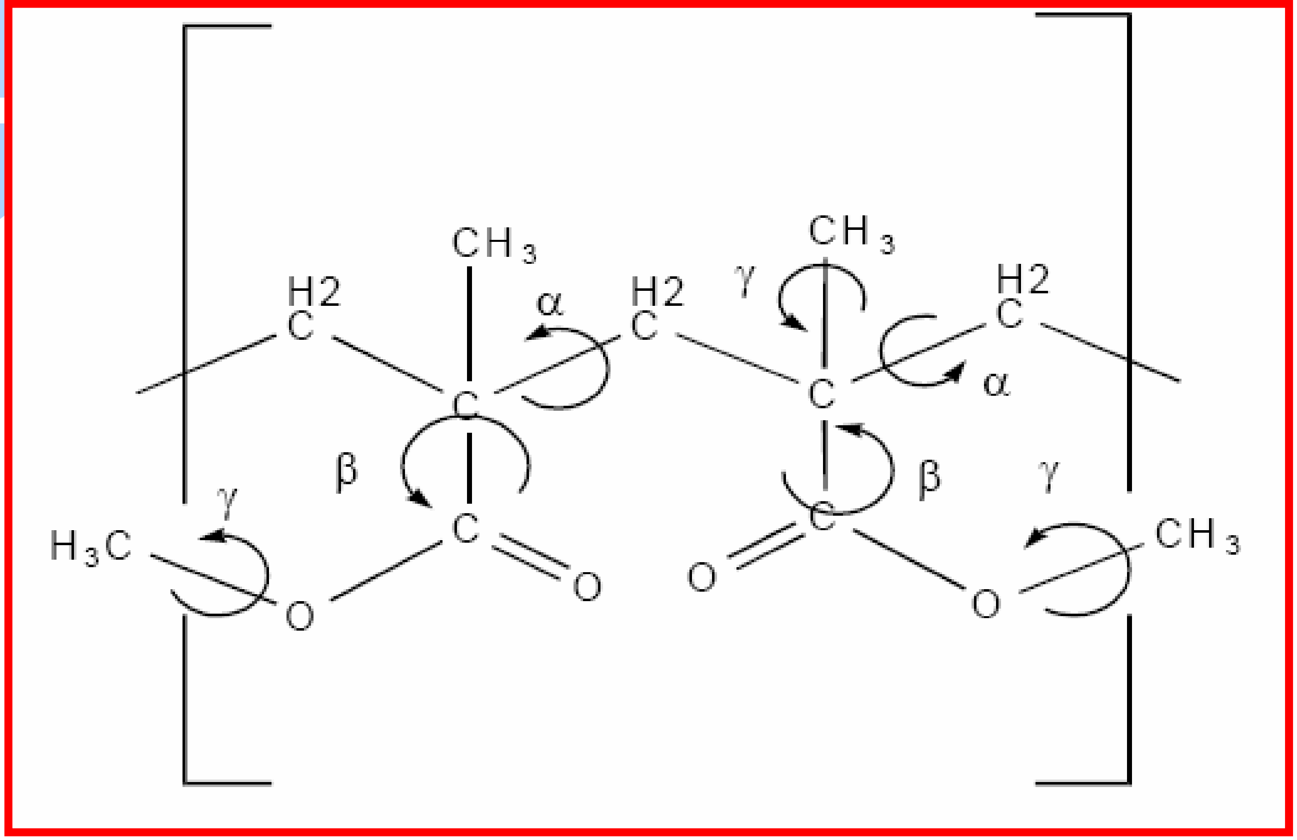
Glass-Rubber Transition Behavior

Table: Multiple Transitions in Amorphous Polystyrene (26)

Temperature	Transitions	Suggested Mechanisms
433°K (160°C)	$T_{1,1}$	Liquid$_1$ → liquid$_2$
373°K (100°C)	T_g	Long-range chain motions
325 ± 4°K (~ 50°C)	β	Torsional vibrations of phenyl groups
130°K	γ	Motions due to four carbon backbone moieties
38–48°K	δ	Oscillation or wagging of phenyl groups

J. E. Guillet, in Photophysical and photochemical tools in Polymer Science, conformation, dynamics and morphology, 1986.

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



Christoff, Atvars, Macromolecules, 1999

how to acess the relaxation processes?

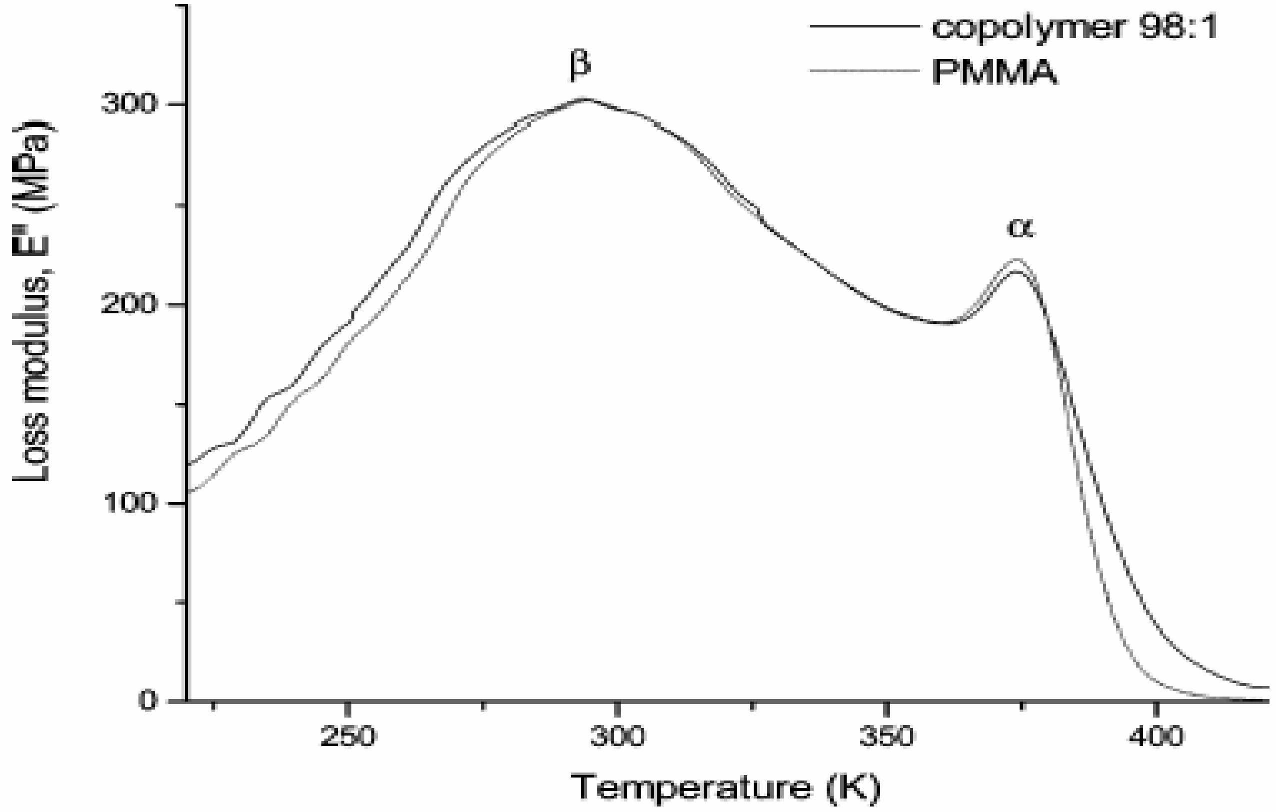


Figure 5. Temperature dependence of loss modulus (E'') for poly(methyl methacrylate) and poly(methyl methacrylate-*co*-9-methylanthryl methacrylate) (98:1). Frequency = 3.3 Hz.

Several techniques: DSC, DMTA, RMN, fluorescence pectroscopy,

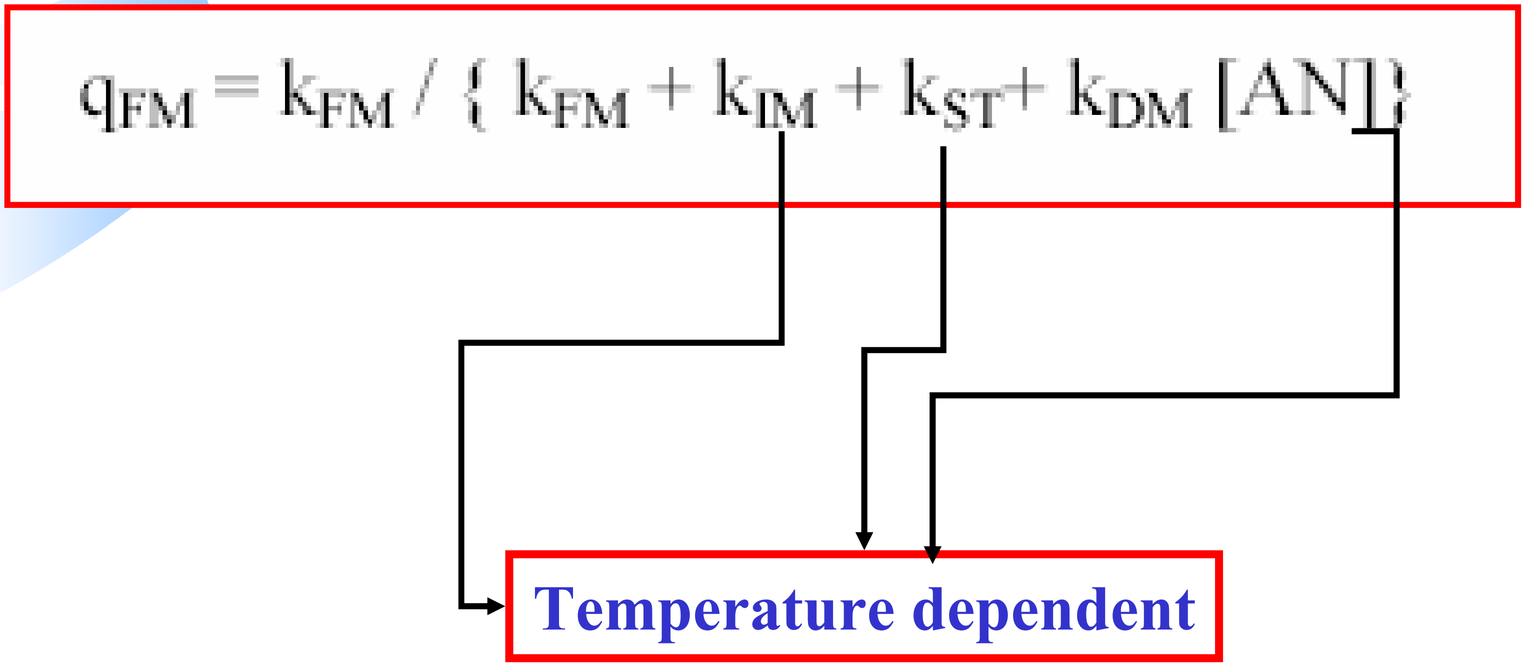
De Deus, et al. Macromolecules, 2005 etc

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

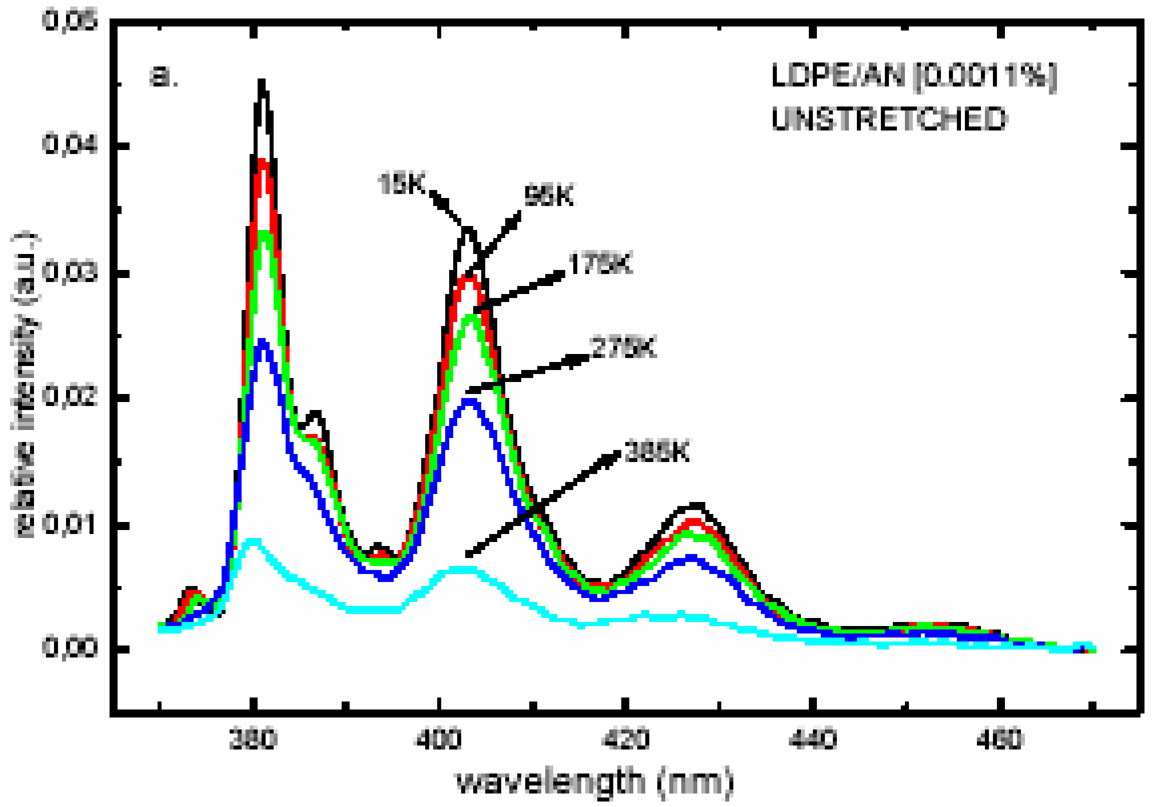


$$q_{FM} = k_{FM} / \{ k_{FM} + k_{IM} + k_{ST} + k_{DM} [AN] \}$$

Temperature dependent

$$\ln [(I_F^0 / I_F) - 1] = A - E_a/RT$$

Example: anthracene in low density polyethylene



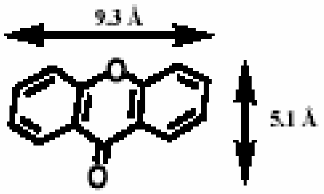
Talhavini et al., Polymer 1996

Example of steady state phosphorescence versus temperature

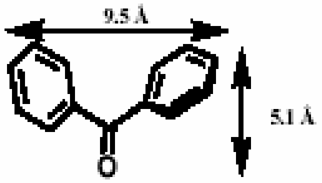
$$\phi_{Ph} = \phi_{ST}\left[k_{Ph}/(k_{Ph} + k_{nr})\right]$$

$$1/I_P - 1/I_0 = B\exp(-E_a/RT)$$

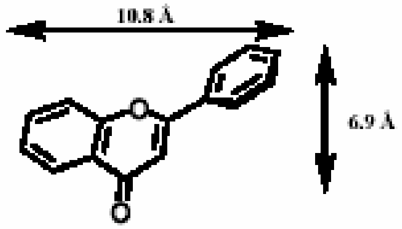
Phosphorecence of flavones in acrylates and polystyrene



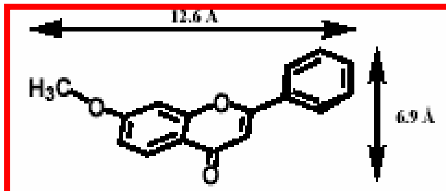
Xanthone (Xt)



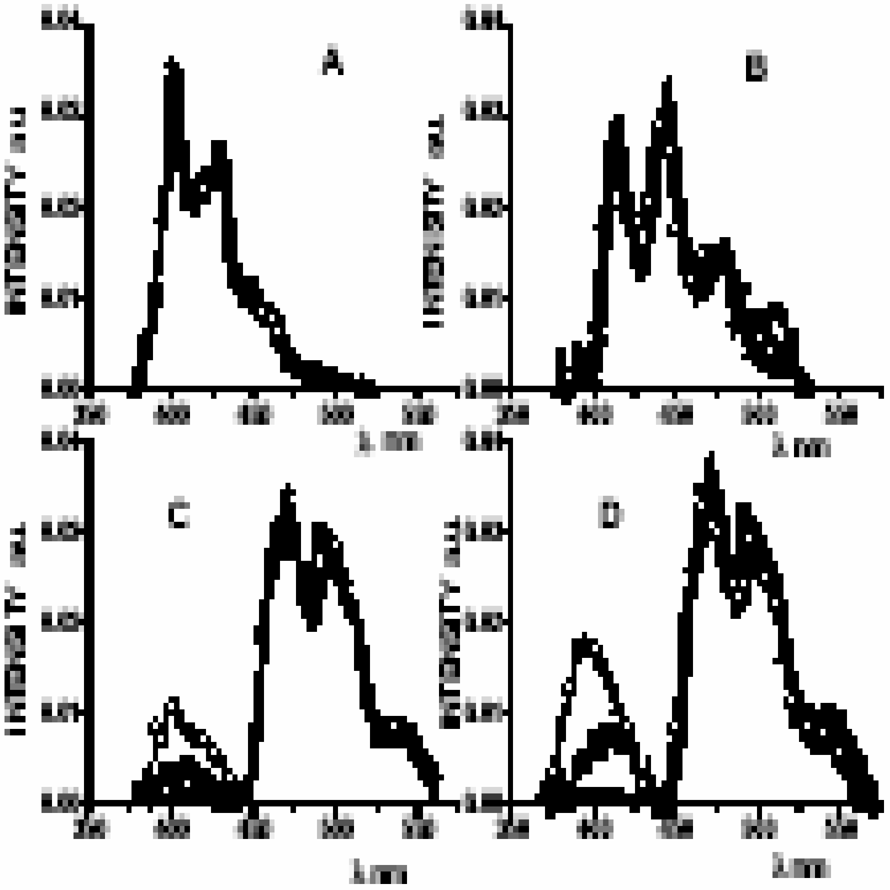
Benzophenone (Bp)



Flavone (F0)



7-Methoxyflavone (F7)



In PS

Christoff, Atvars, Macromolecules, 1999

Phosphorecence in acrylates and polystyrene

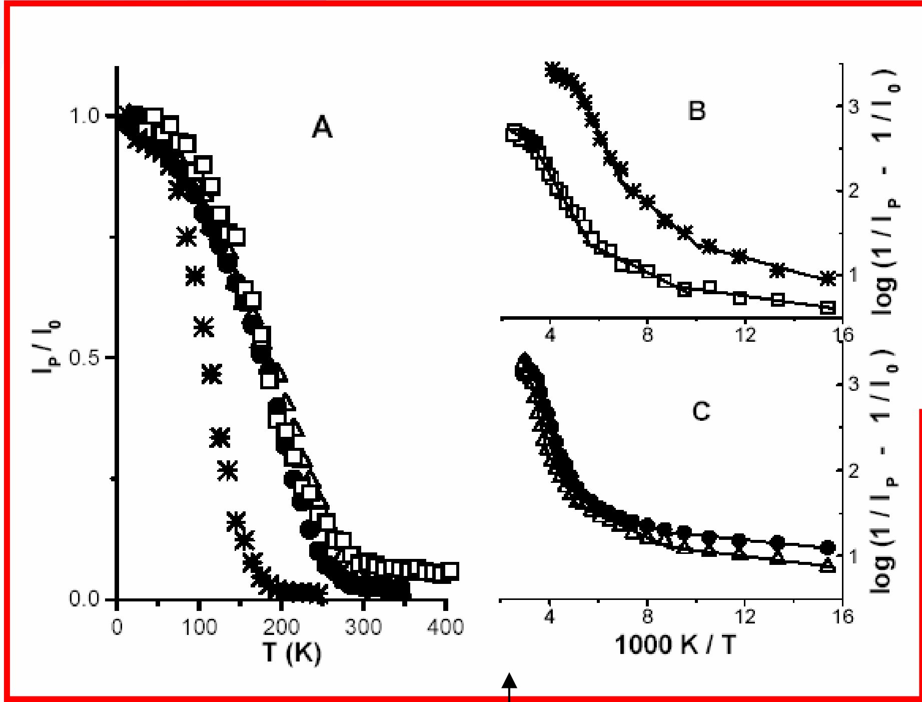
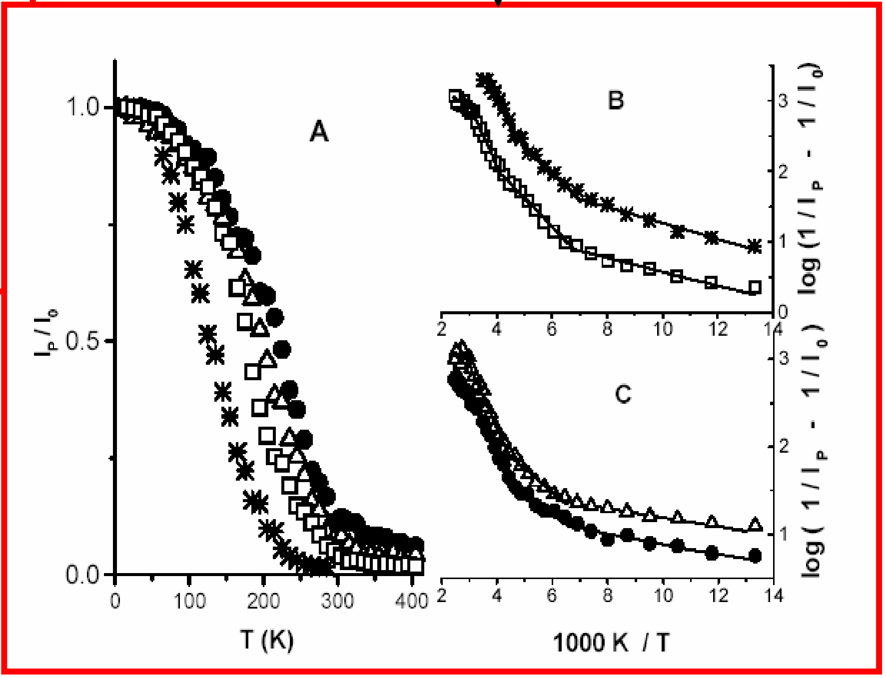


Figure 2. **A**. Temperature dependence of the normalized phosphorescence intensity of probes in PS films. Arrhenius plots for I_P x 1/T for: **B**. Xt (✳) and Bp (❑); **C**. F0 (●), and F7(□). I_0 was taken as 15 K.

Figure 3. **A**. Temperature dependence of the normalized phosphorescence intensity of probes in PMMA films. Arrhenius plots for I_P x 1/T for: **B**. Xt (✳) and Bp (❑); **C**. F0 (●), and F7(□). I_0 was taken as 15 K.



Christoff, Atvars, Macromolecules, 1999

Activation energies for relaxaton processes by phosphorescence emission

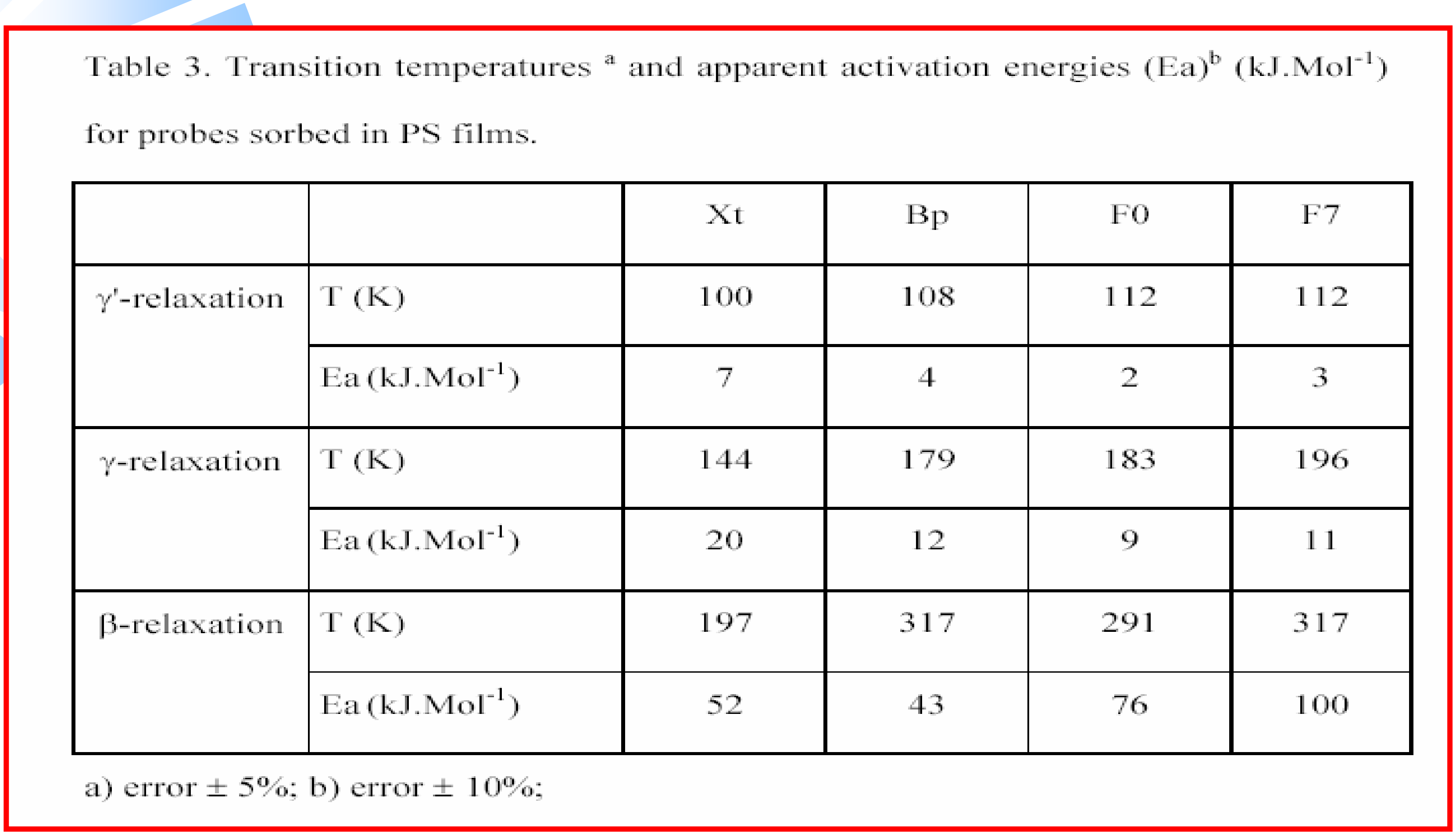


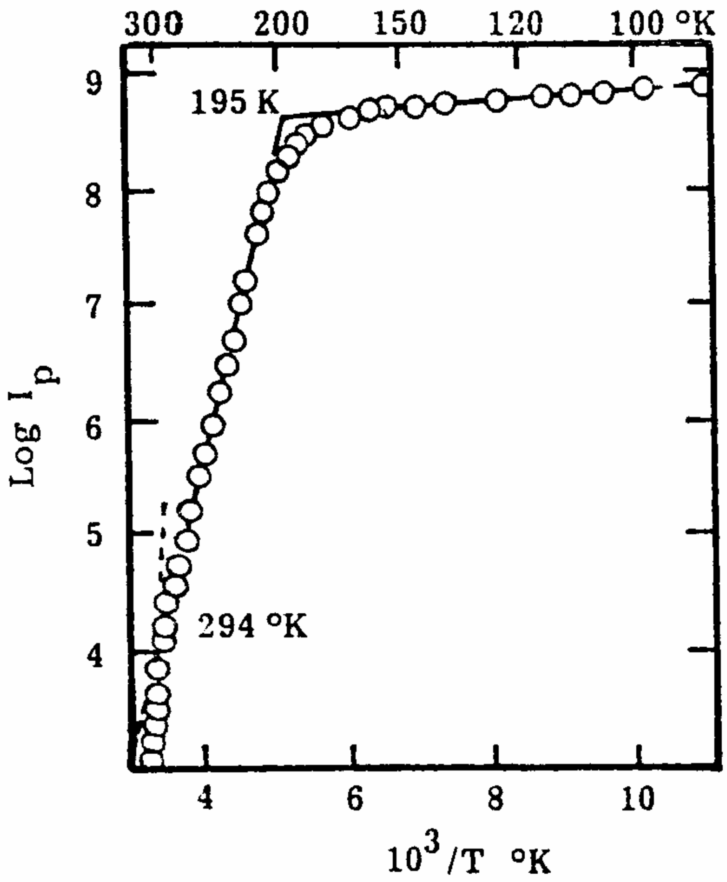
Table 3. Transition temperatures [a] and apparent activation energies (Ea)[b] (kJ.Mol^{-1}) for probes sorbed in PS films.

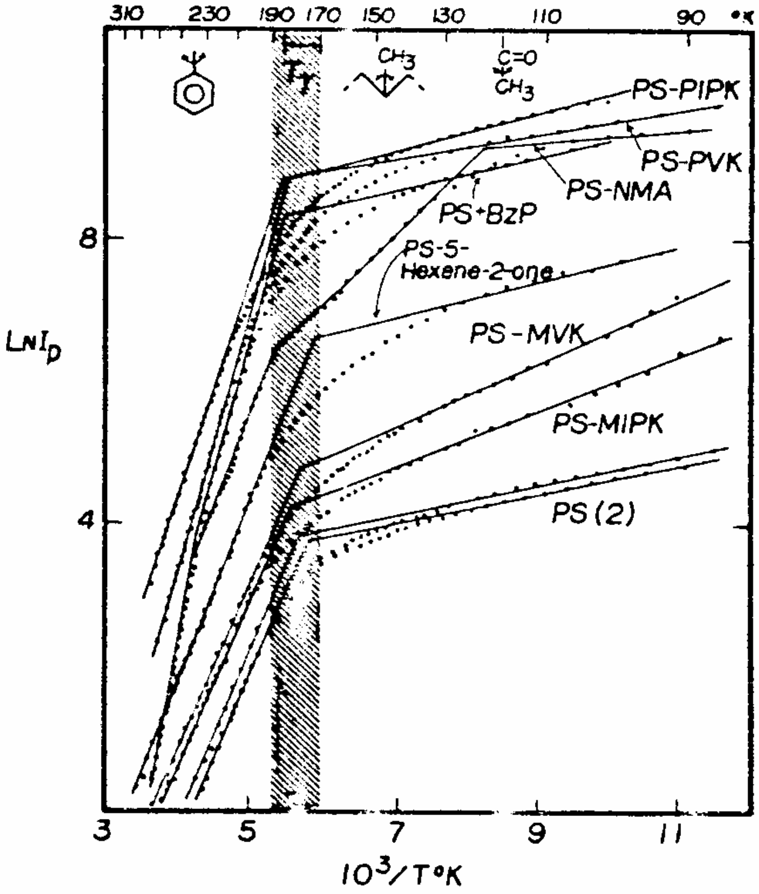
		Xt	Bp	F0	F7
γ'-relaxation	T (K)	100	108	112	112
	Ea (kJ.Mol^{-1})	7	4	2	3
γ-relaxation	T (K)	144	179	183	196
	Ea (kJ.Mol^{-1})	20	12	9	11
β-relaxation	T (K)	197	317	291	317
	Ea (kJ.Mol^{-1})	52	43	76	100

a) error ± 5%; b) error ± 10%;

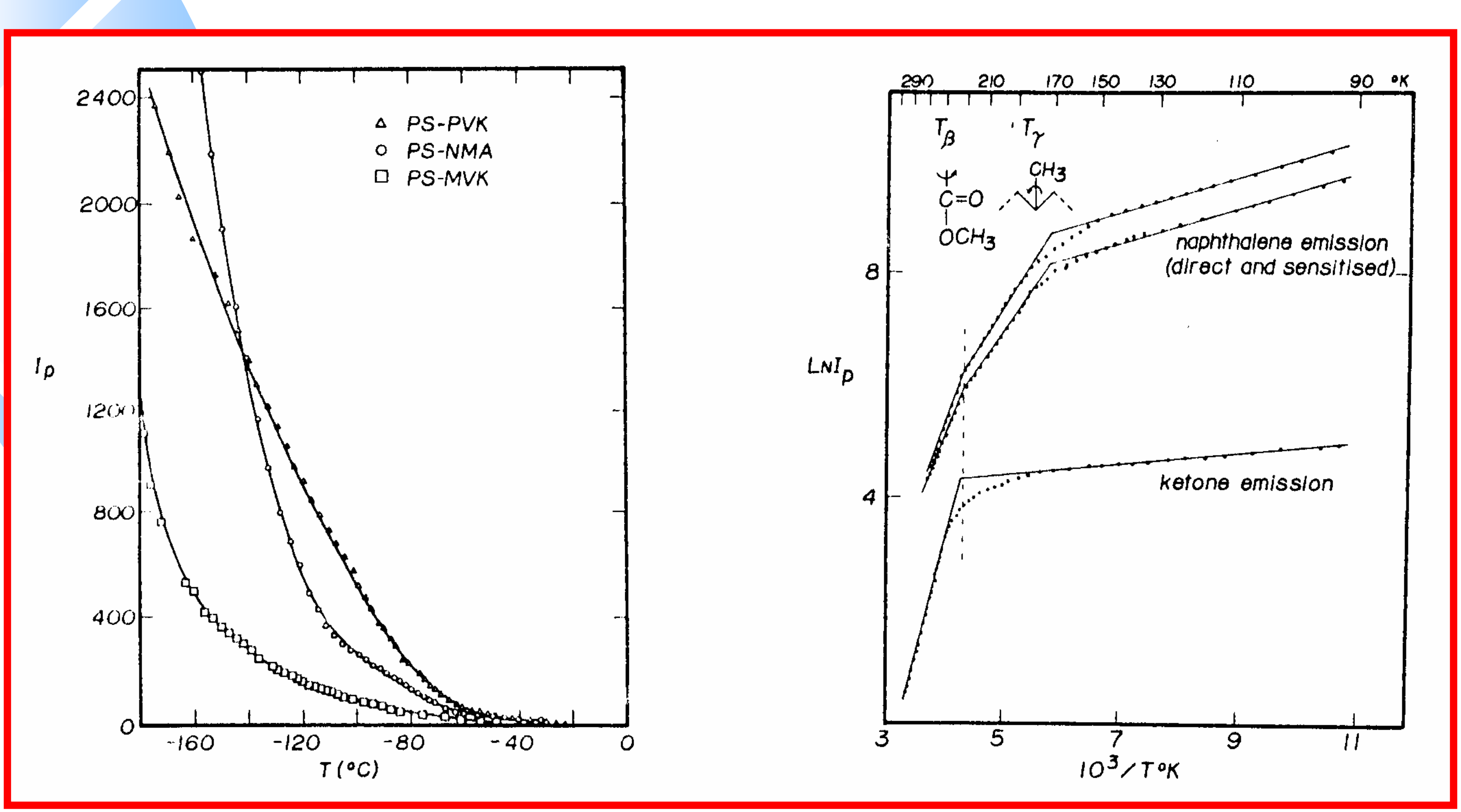
Christoff, Atvars, Macromolecules, 1999

Steady state phosphorescence emission versus temperature – several examples

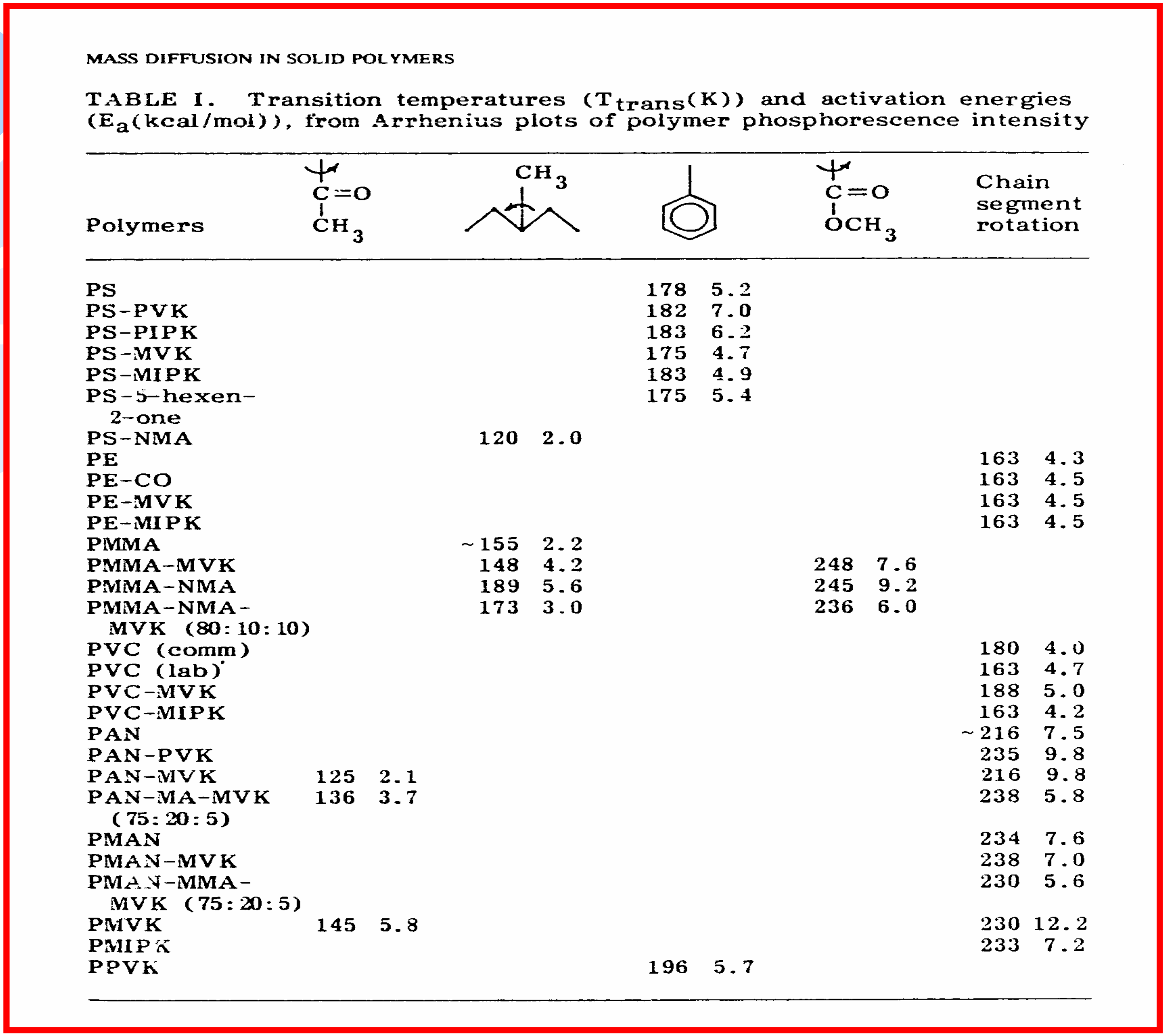




J. E. Guillet, in Photophysical and photochemical tools in Polymer Science, conformation, dynamics and morphology, 1986.



J. E. Guillet, in Photophysical and photochemical tools in Polymer Science, conformation, dynamics and morphology, 1986.



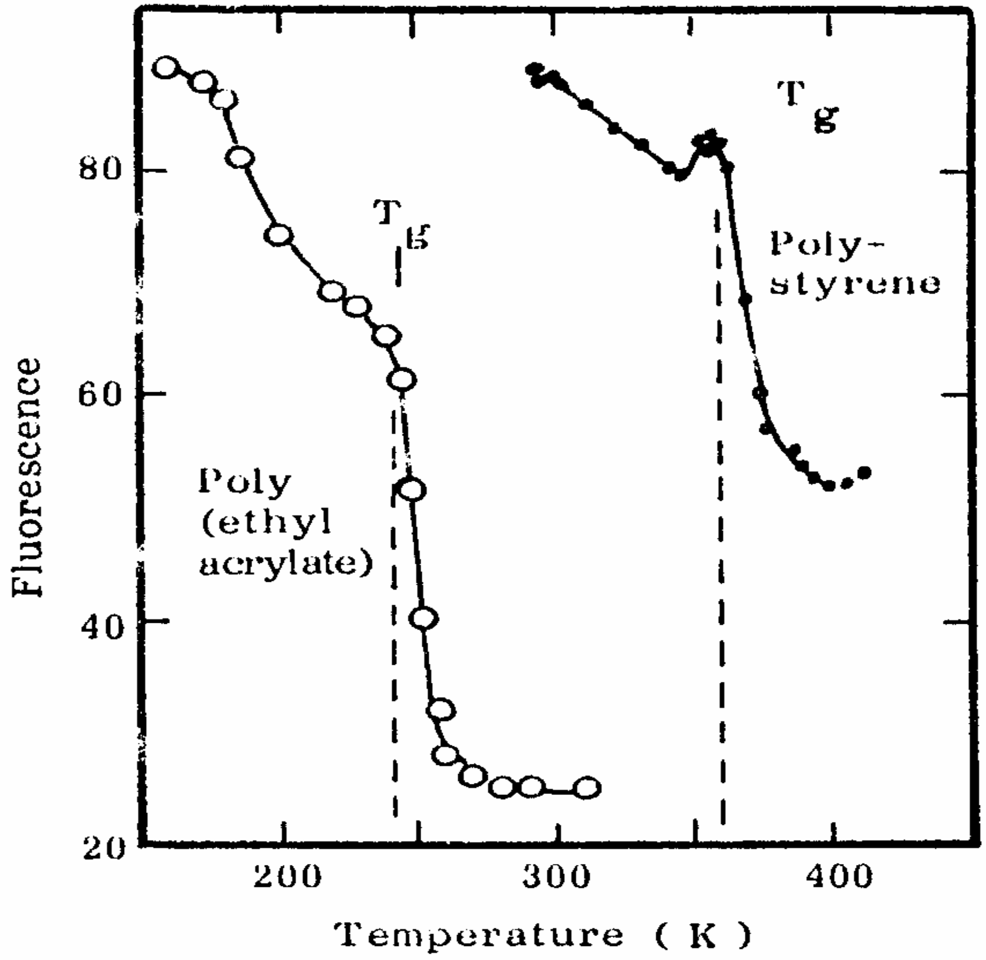
MASS DIFFUSION IN SOLID POLYMERS

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

Polymers	C=O CH_3		CH_3				C=O OCH_3		Chain segment rotation	
PS					178	5.2				
PS-PVK					182	7.0				
PS-PIPK					183	6.2				
PS-MVK					175	4.7				
PS-MIPK					183	4.9				
PS-5-hexen-2-one					175	5.4				
PS-NMA			120	2.0						
PE									163	4.3
PE-CO									163	4.5
PE-MVK									163	4.5
PE-MIPK									163	4.5
PMMA			~155	2.2						
PMMA-MVK			148	4.2			248	7.6		
PMMA-NMA			189	5.6			245	9.2		
PMMA-NMA-MVK (80:10:10)			173	3.0			236	6.0		
PVC (comm)									180	4.0
PVC (lab)									163	4.7
PVC-MVK									188	5.0
PVC-MIPK									163	4.2
PAN									~216	7.5
PAN-PVK									235	9.8
PAN-MVK	125	2.1							216	9.8
PAN-MA-MVK (75:20:5)	136	3.7							238	5.8
PMAN									234	7.6
PMAN-MVK									238	7.0
PMAN-MMA-MVK (75:20:5)									230	5.6
PMVK	145	5.8							230	12.2
PMIPK									233	7.2
PPVK					196	5.7				

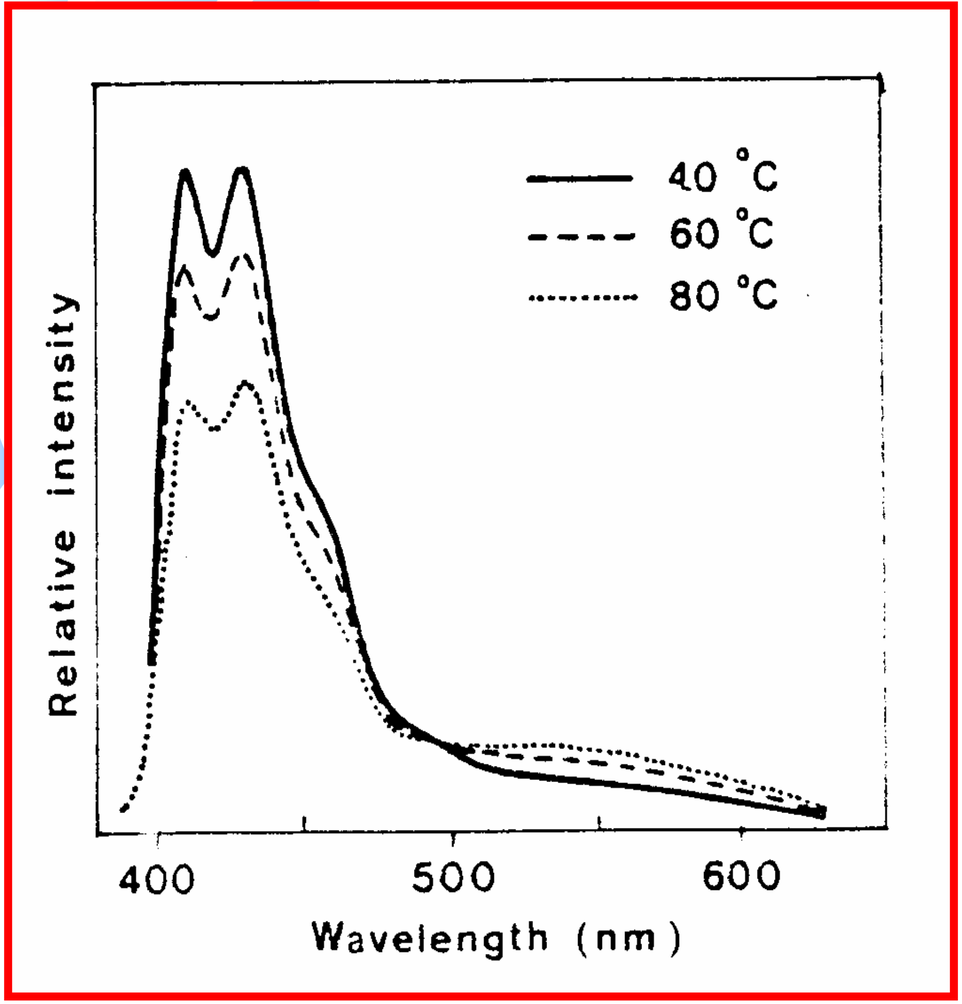
J. E. Guillet, 1986

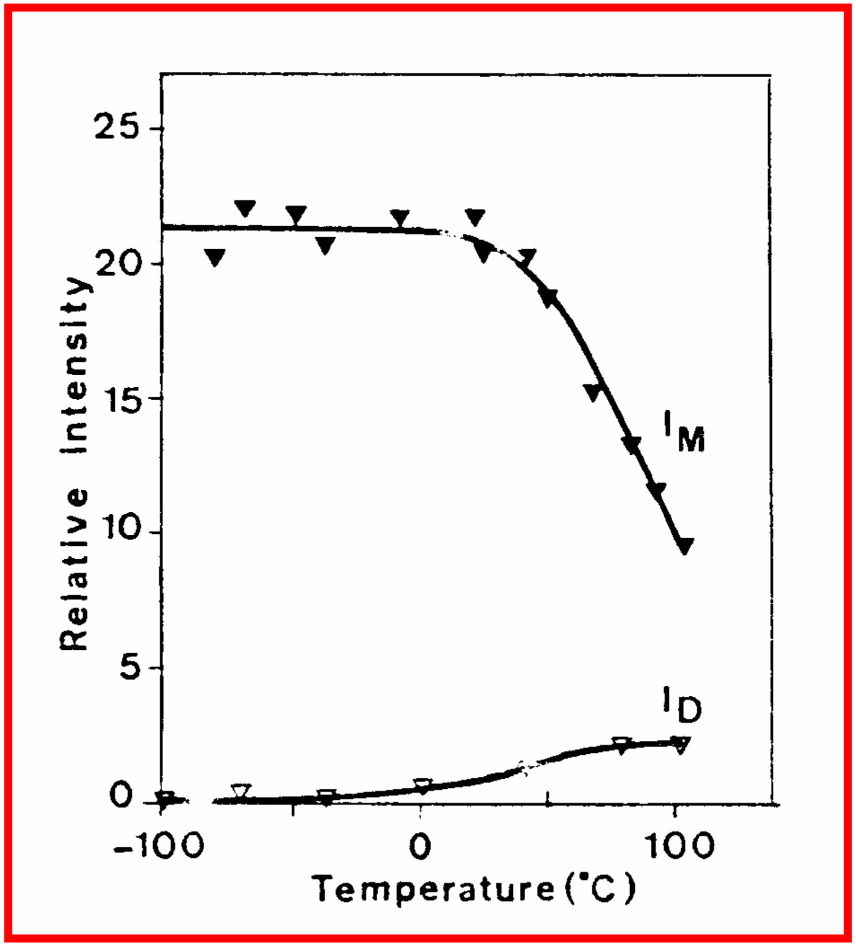
Using quenching processes of phosphorescence: diffusion of oxygen in polymers



J. E. Guillet, in Photophysical and photochemical tools in Polymer Science, conformation, dynamics and morphology, 1986.

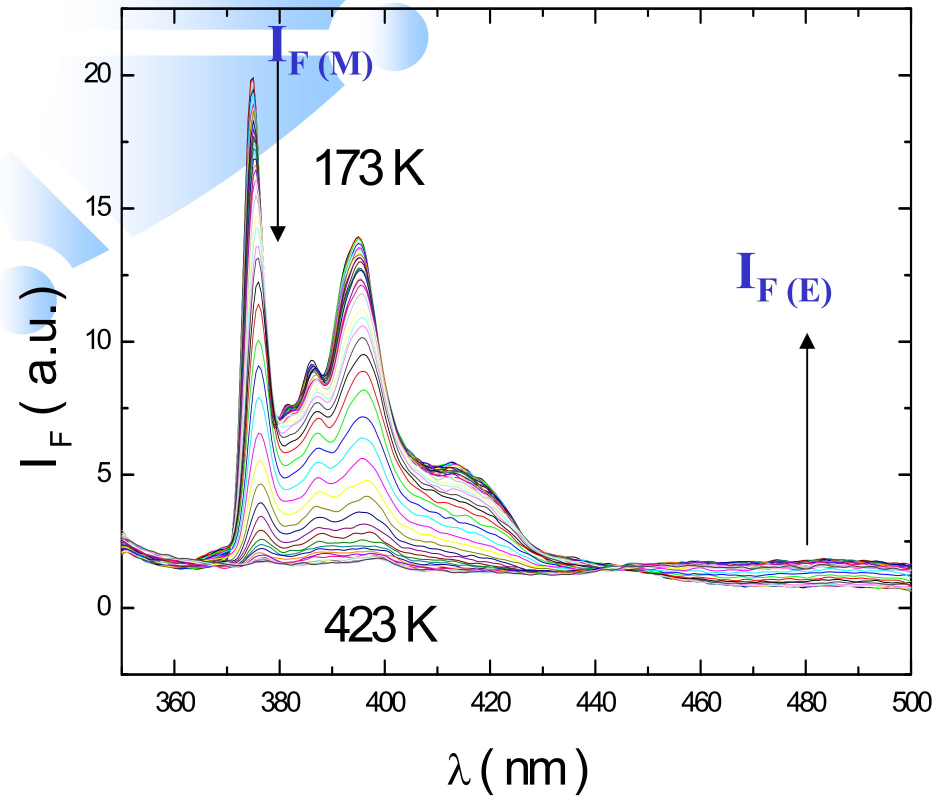
Using excimer emission – example: diphant in polybutadiene

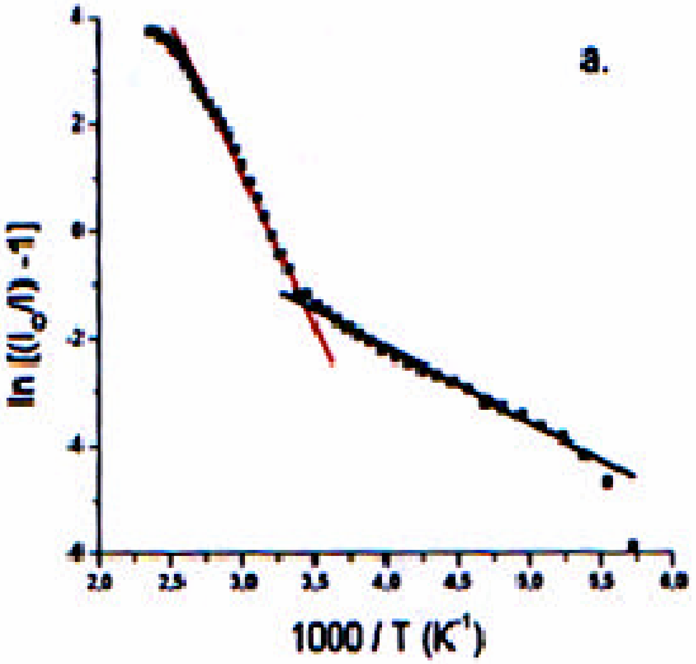




Bokobza et al.: in Photophysical and photochemical tools in Polymer Science, conformation, dynamics and morphology, 1986.

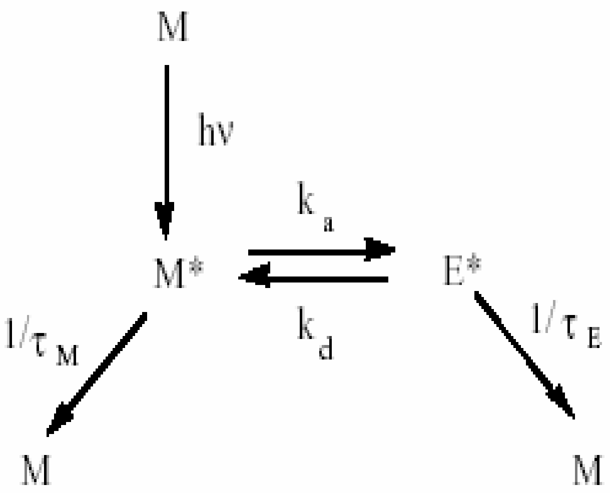
Using excimer emission – example: 1,3-dipyrenyl propane in low density polyethylene

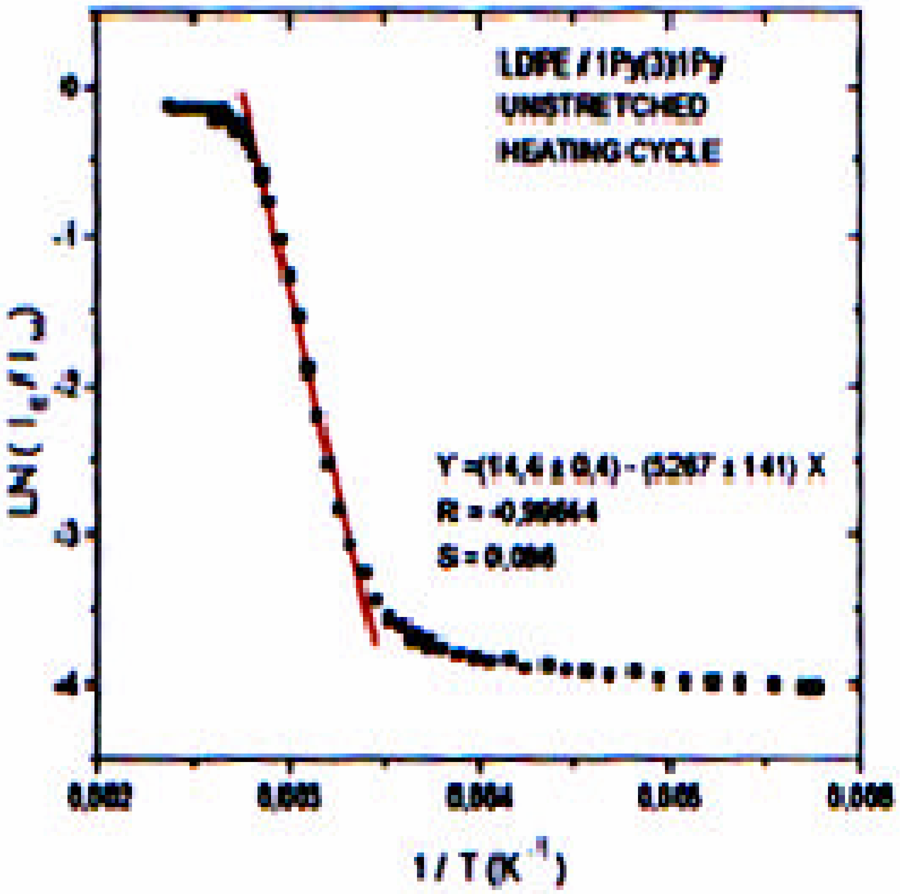




Vigil et al. Curr. Org. Chem. 2003.

1,3-dipyrenyl propane in LDPE





Vigil et al. Curr. Org. Chem. 2003.

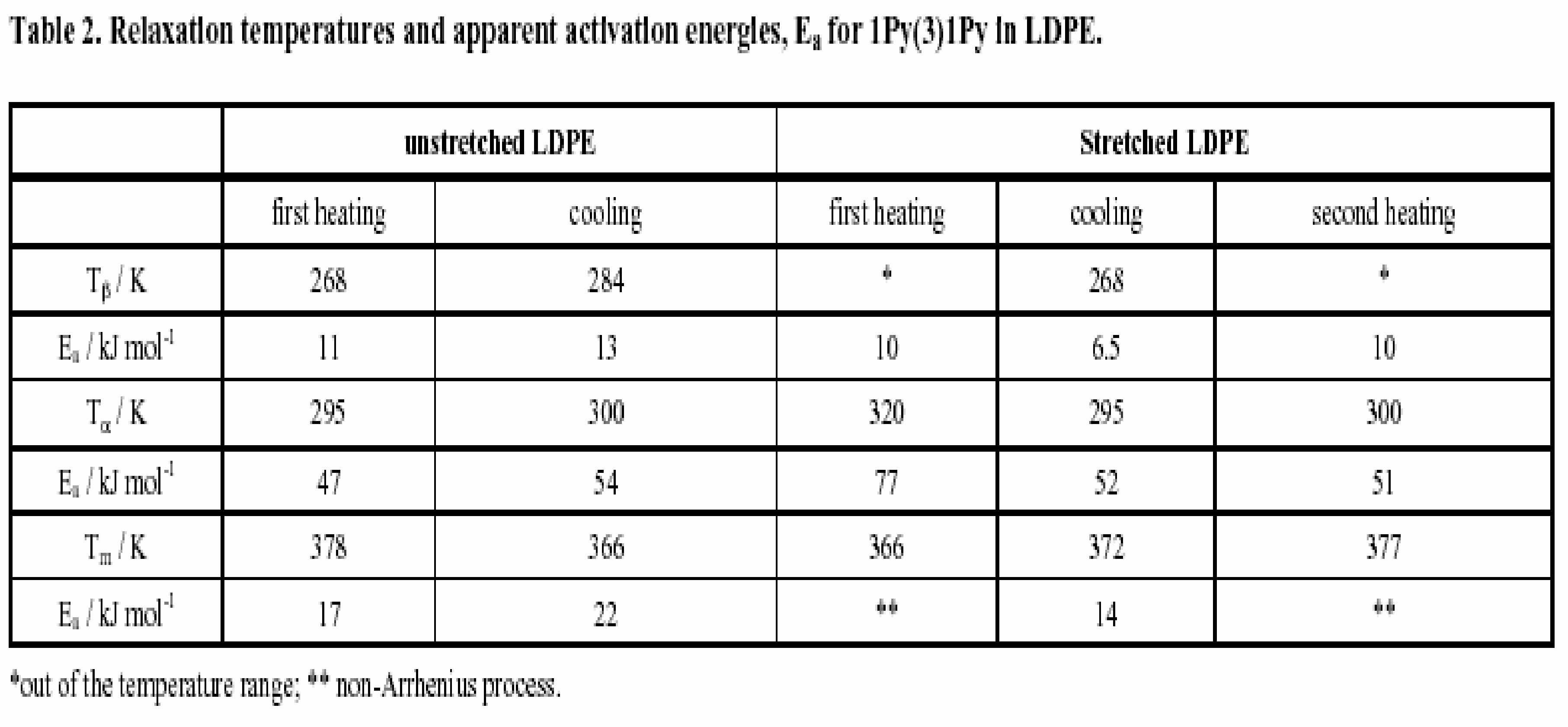
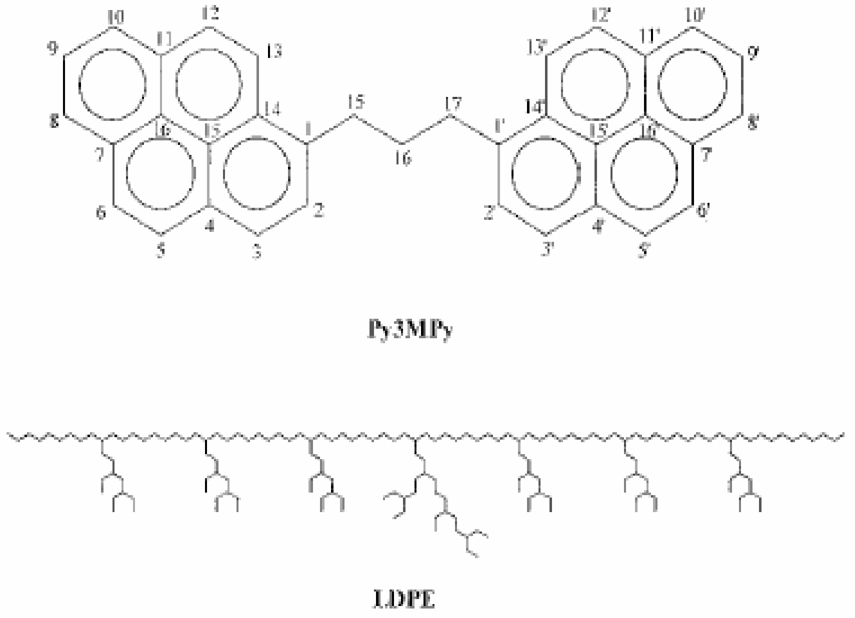


Table 2. Relaxation temperatures and apparent activation energies, E_a for 1Py(3)1Py in LDPE.

	unstretched LDPE		Stretched LDPE		
	first heating	cooling	first heating	cooling	second heating
T_β / K	268	284	*	268	*
E_a / kJ mol^{-1}	11	13	10	6.5	10
T_α / K	295	300	320	295	300
E_a / kJ mol^{-1}	47	54	77	52	51
T_m / K	378	366	366	372	377
E_a / kJ mol^{-1}	17	22	**	14	**

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

Dynamic of the relaxation



Py3MPy

LDPE

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

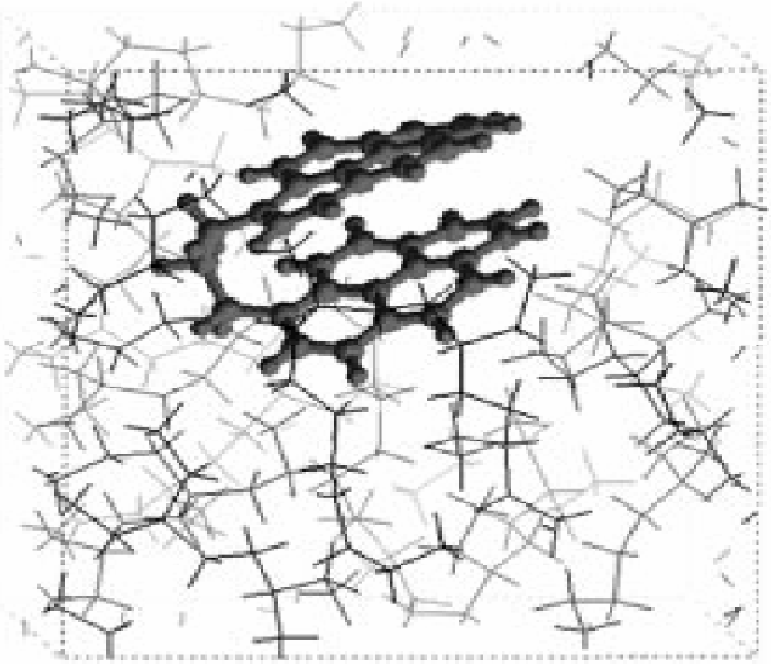
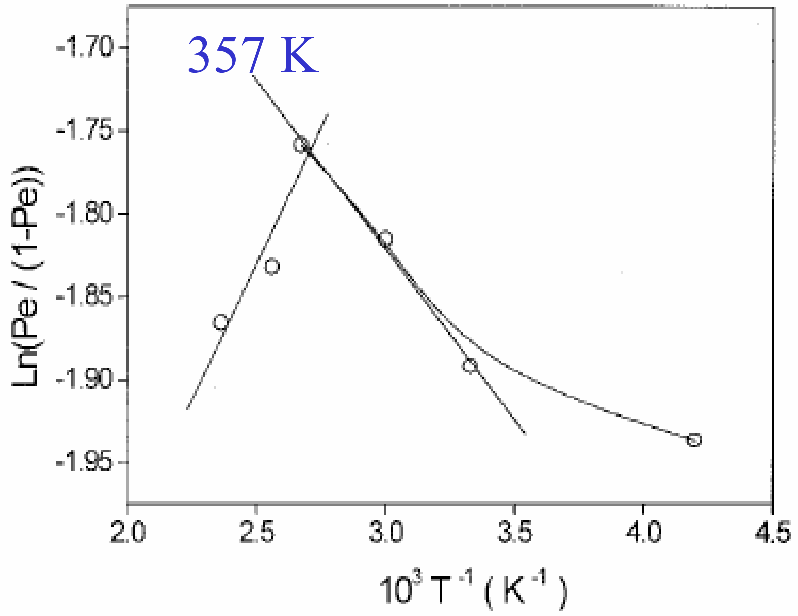


Figure 9. Illustration of an excimer conformation of Py3MPy adsorbed into the LDPE matrix.

Pozuelo, et al. Macromol. Theor. Simul., 2001



357 K

Figure 7. Variation of ln[P_E/(1−P_E)] vs. T^{-1} for Py3MPy adsorbed into the LDPE matrix.

α-relaxation

β-relaxation process

Melting point (DSC)

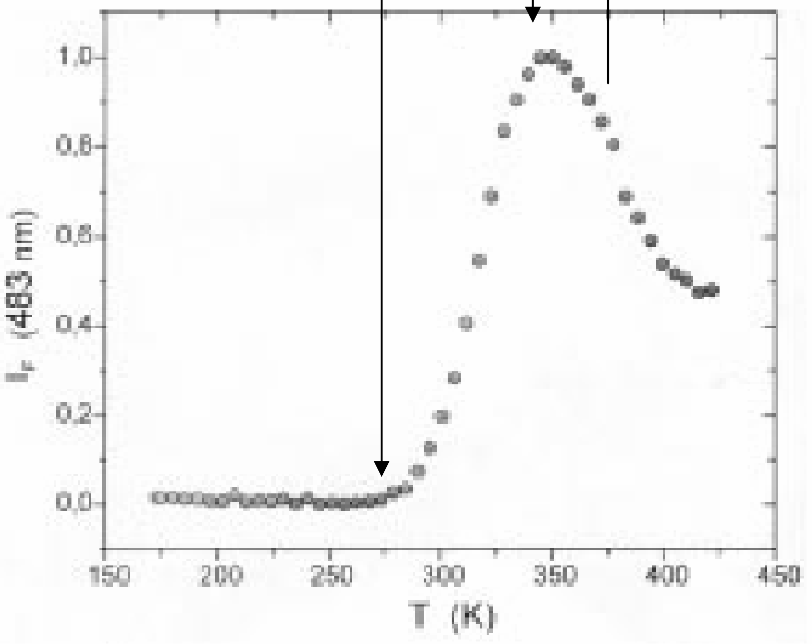
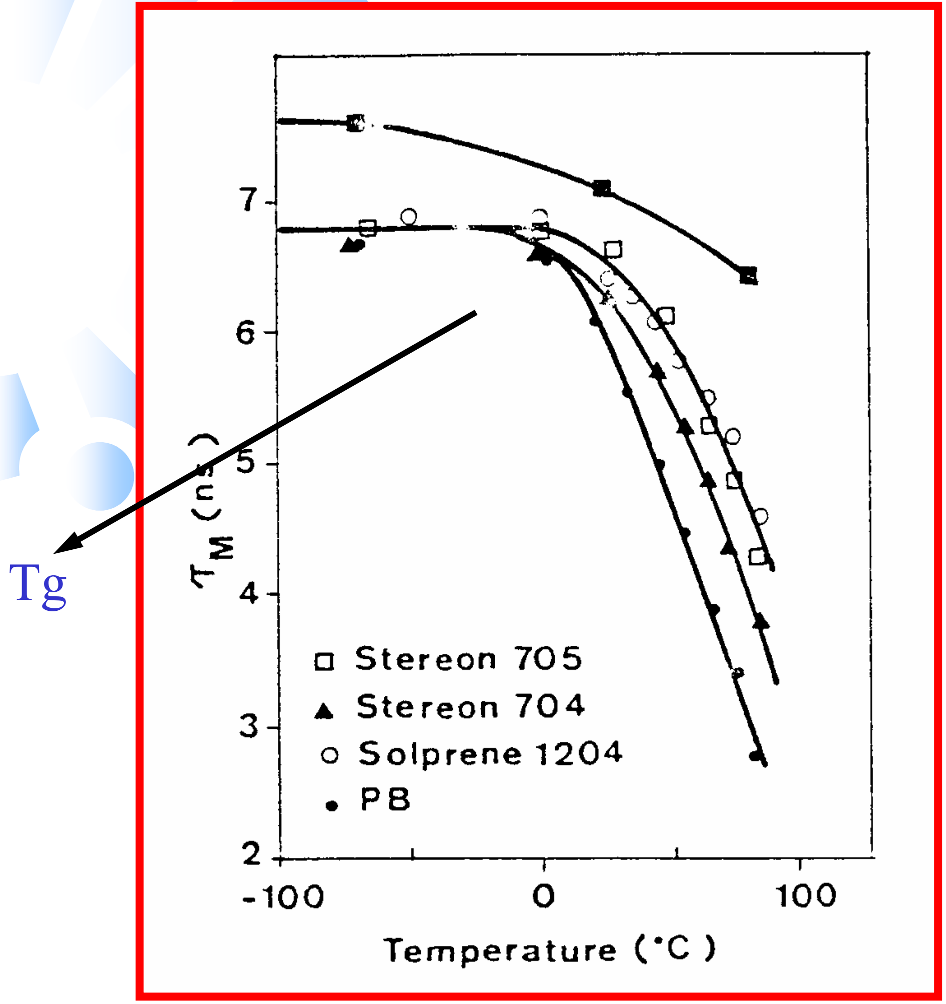
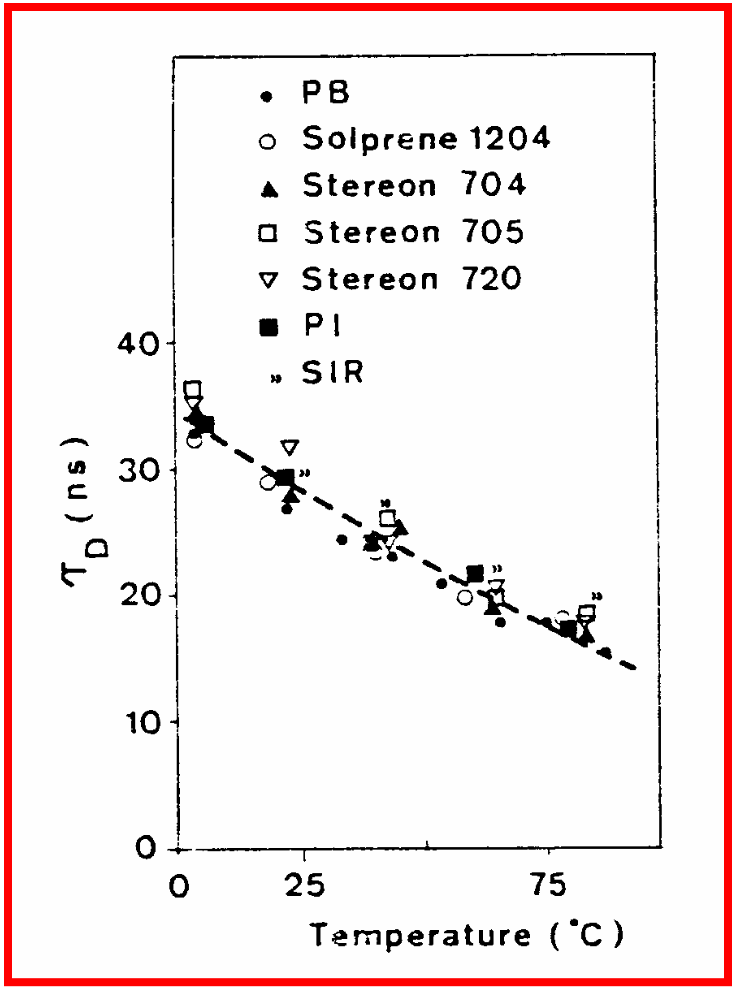


Figure 8. Excimer fluorescence intensity of Py3MPy in the LDPE matrix (adapted from ref.[3]).

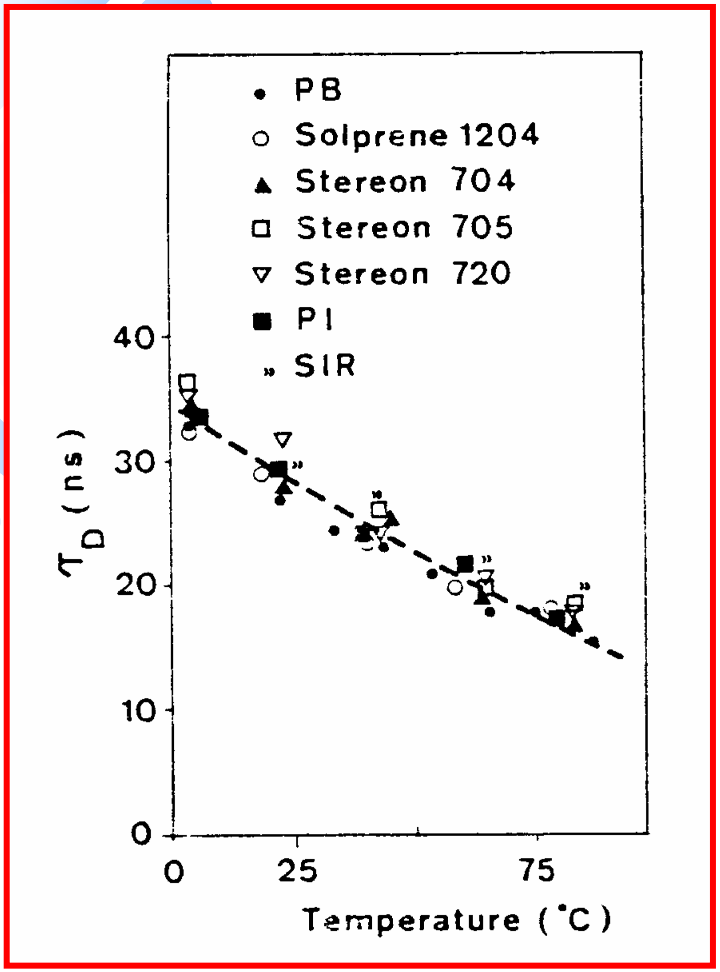
Pozuelo, et al. Macromol. Theor. Simul., 2001

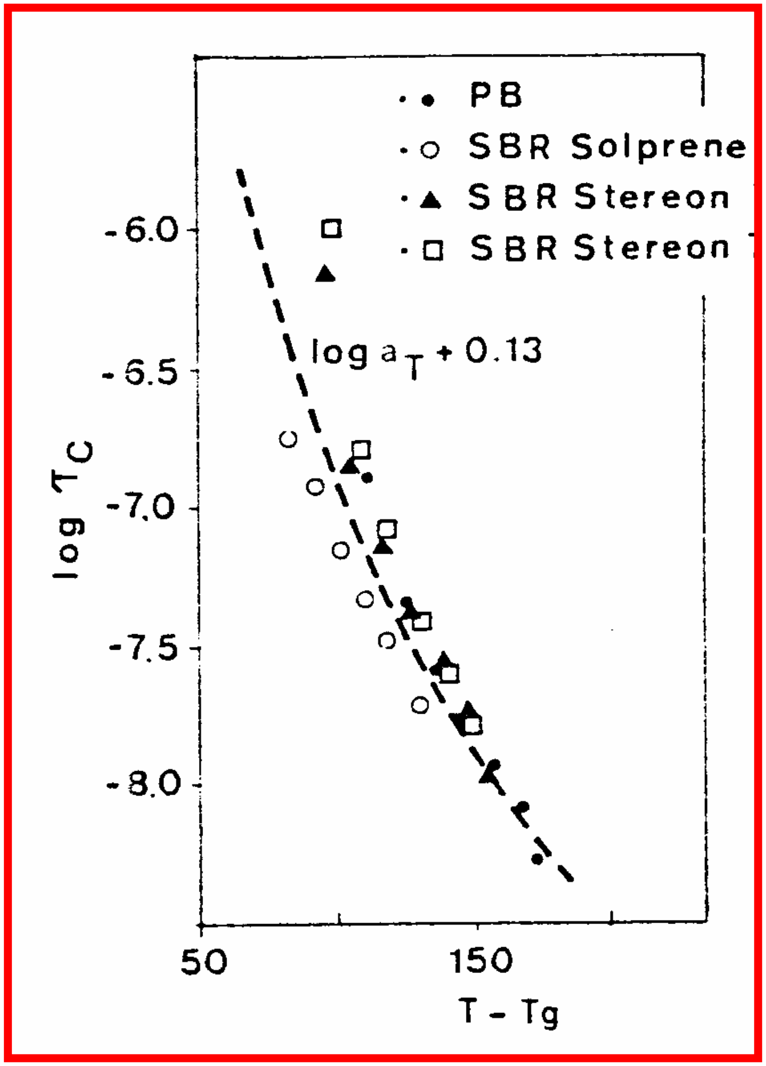
Time resolved spectroscopy – example: Diphant in poly(butadiene) and copolymers with styrene





Bokobza et al.: in Photophysical and photochemical tools in Polymer Science, conformation, dynamics and morphology,1986.





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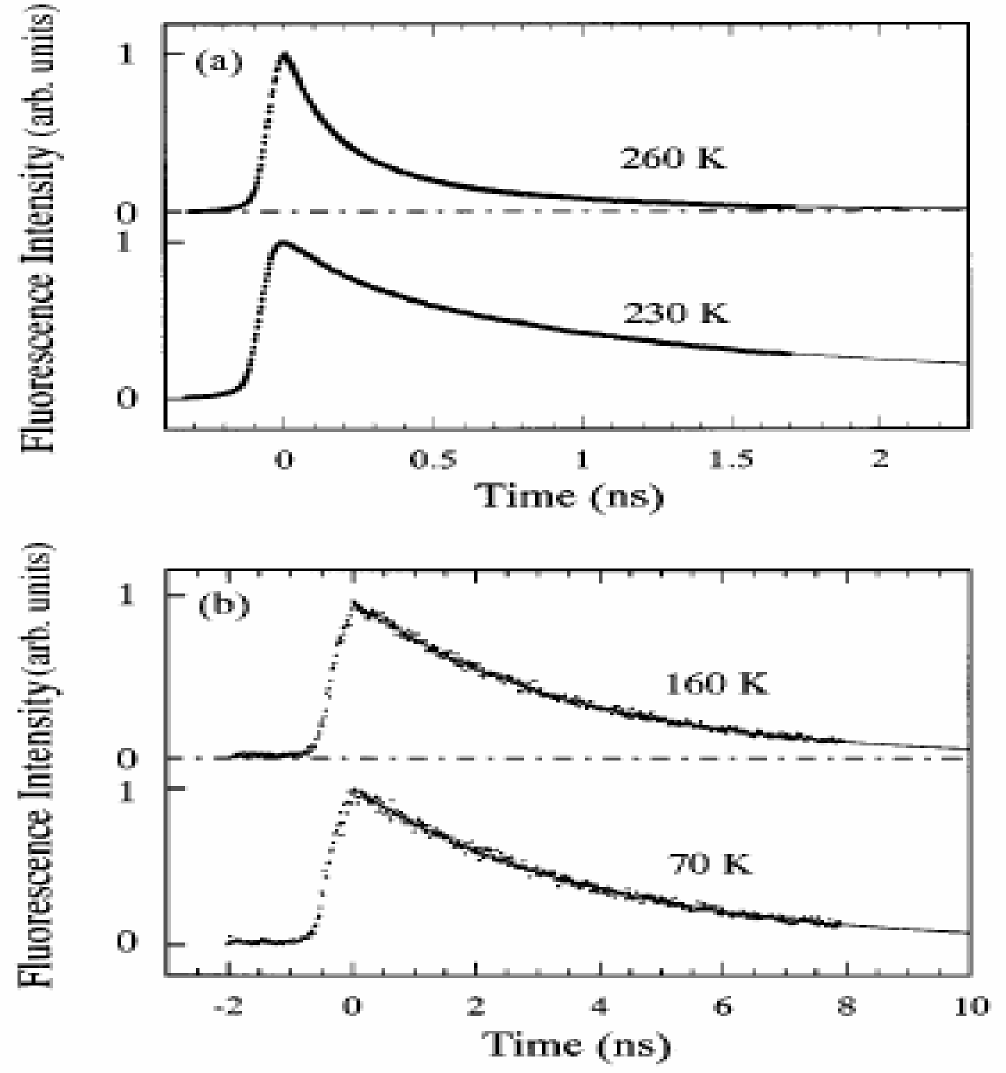


FIG. 2. Fluorescence decay curves of MG doped in PB measured by using the two experimental systems described in the text. Dots are the experimentally obtained data, and solid lines are fitting curves. (a) In the higher-temperature region biexponential decay is found. (b) In the lower-temperature region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

Malachite green in polybutadiene

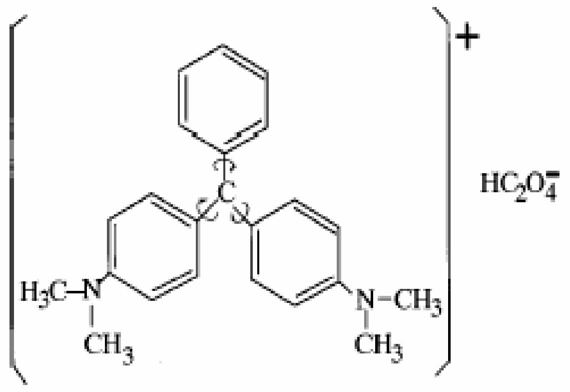


FIG. 1. Molecular structure of malachite green

J. Y. Ye e al., Phys. Rev. B, 1997

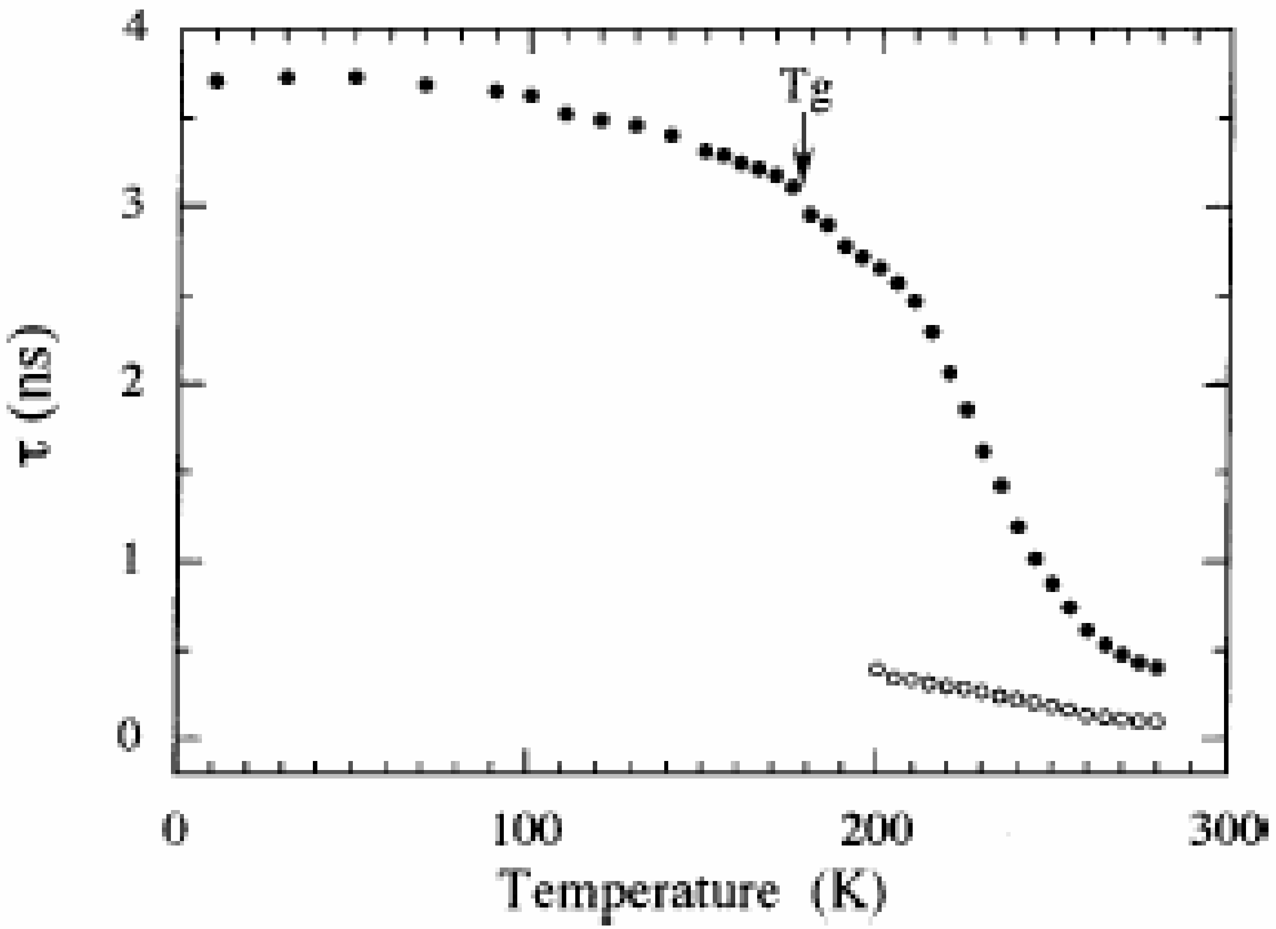


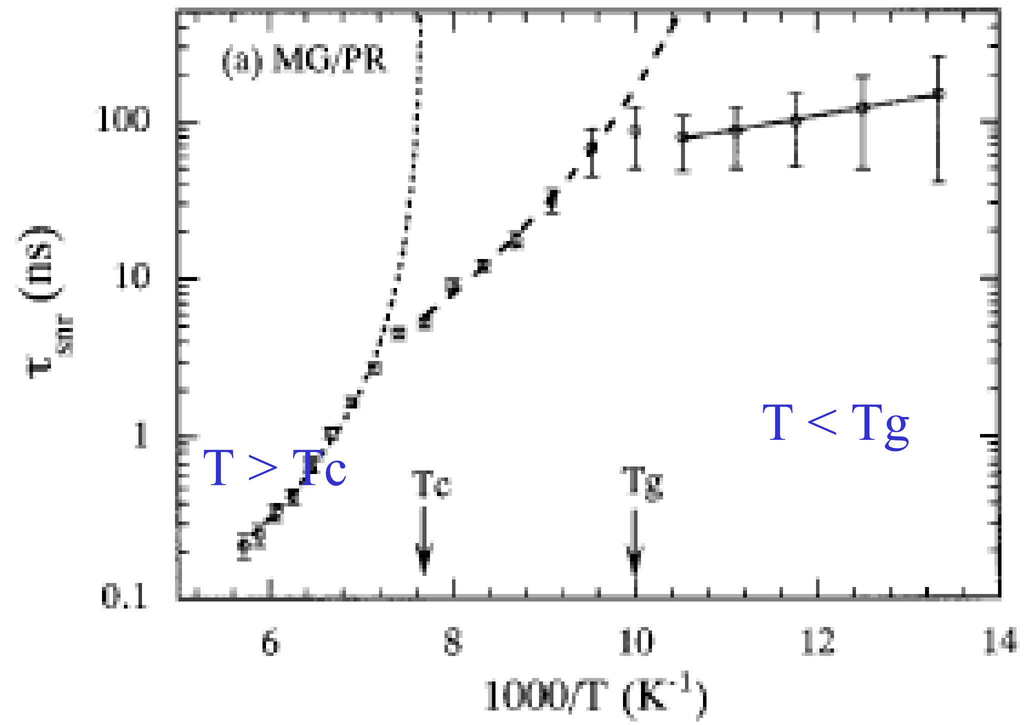
FIG. 5. Temperature dependence of the fluorescence lifetime of MG in PB.

J. Y. Ye e al., Phys. Rev. B, 1997

$$\tau_{snr} = \tau_H^0 [T_c/(T-T_c)]^{\gamma} \quad \text{for } T > T_c,$$

$$\tau_{snr} = \tau_M^0 \exp[B/(T-T_0)] \quad \text{for } T_c > T > T_g,$$

$$\tau_{snr} = \tau_L^0 \exp[E_a/k_B T] \quad \text{for } T < T_g,$$



J. Y. Ye e al., Phys. Rev. B, 1997

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**

outline

☐ 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