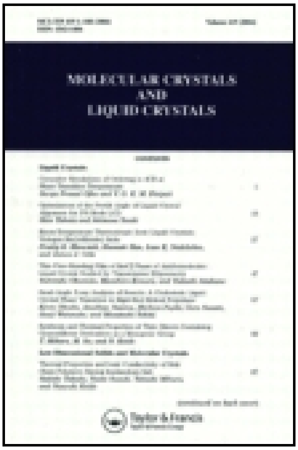

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Relationships Between the Electron-Phonon Coupling and the Elastic Properties of Polymer Matrices: A Hole-Burning Study

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RELATIONSHIPS BETWEEN THE ELECTRON-PHONON COUPLING AND THE ELASTIC PROPERTIES OF POLYMER MATRICES: A HOLE-BURNING STUDY

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Abstract Spectral holes have been investigated between 7 and 50K on tetra-*tert*-butyl-tetra-azaporphine(*t*-Bu-TAP) embedded in a number of polymers. The maximum position(ν_{ph}) of the pseudo wing and the temperature dependence of the quasi-homogeneous hole width(Γ_{qh}) have been measured and compared to the known values of the Young's modulus(E') of the matrix. We found that in polymers with larger E' the ν_{ph} is higher and the hole width is smaller. The influence of the dynamic mechanical properties as well as the polarity and hydrogen bonding on intermolecular vibronic coupling is discussed.

INTRODUCTION

The electron-phonon coupling of optical transitions of the impurity centers at low temperatures should be closely related to mechanical, acoustical and thermodynamical characteristics of the solid matrix.[1] In case of organic amorphous systems such relationships have not been investigated in detail so far. On the other hand, in several hole burning experiments a pronounced dependence of quasihomogeneous hole widths(Γ_{qh}) on the host matrix has been observed.[2,3] Γ_{qh} measured in porphine between 1 and 5K vary by more than an order of magnitude within a set of seven polymers.[2] Phthalocyanine doped in polyethylene, poly(methyl methacrylate) and polystyrene has the Γ_{qh} values at 10K of ~1, 6 and 13GHz, respectively.[3] At the same time, it was observed that the distance between the 0-0 hole and the maximum of the broad pseudo-wing(ν_{ph}) can be fairly different in various polymers.[4,5] As expected, the characteristic frequencies of optically active low-energy modes strongly influence the temperature dependence of the Debye-Waller factor.[4]

In this work, the pseudo-phonon side band and the temperature dependence of Γ_{qh} have been studied in a set of about 20 polymers. Tetra-*tert*-butyl-tetra-azaporphine(*t*-Bu-

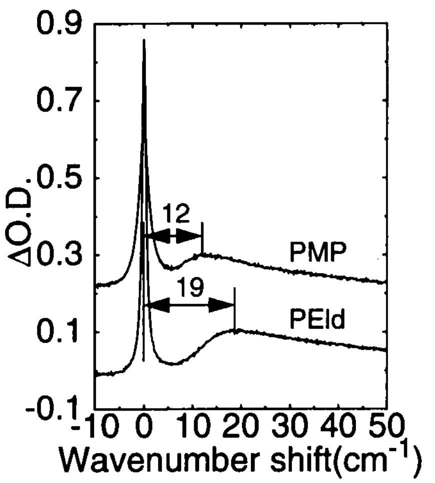
TAP) was chosen as an impurity molecule, since its good solubility as well as the chemical and thermal inertness enables one to dope it in most of the polymeric hosts. It will be shown that in the temperature range T=8-50K both ν_{ph} and Γ_{qh} are correlated with elastic properties of the bulk matrix taken from refs 6 and 7.

EXPERIMENTAL

t-Bu-TAP was used as mixture of randomers.[8] The polymers (Aldrich) were dissolved in a proper solvent (CH_2Cl_2, CF_3CH_2OH, toluene or DMF) upon heating, if necessary, and a small amount of *t*-Bu-TAP was added. The films with optical density of 0.7-1.3 were cast from the solution, dried under vacuum and occasionally hot-pressed. The sample was loaded in the continous flow cryostat (CF1204) supplied with the ITC-4 temperature controller (both Oxford). Holes were burned at the absorption maximum (617-620nm) during 100s with pulse frequency of 100Hz with the aid of a Lambda Physik dye laser LPD 3002E (linewidth 2.5GHz, pulse length ~10ns) pumped with an excimer laser LPX 100. Detection was accomplished in a two-channel set-up using Molectron JD2000 Joulemeter Ratiometer with a sensitive(1kV/mJ) J3S-10 probe in the sample channel and a less sensitive one, J3-09(1V/mJ) as a reference. Γ_{qh} was determined for shallow holes (<5% of absorption change) by means of Lorentzian fitting. The instrumental contribution of 5±0.5GHz was subtracted from the measured hole width.

RESULTS AND DISCUSSION

Bleaching of the molecules via phonon wing absorption under strong irradiation creates a broad pseudo wing on the long-wavelength side of the hole (Figure 1). The absorption minimum in the pseudo-wing region (ν_{ph}) approximately gives the characteristic frequency of low-energy modes which are most strongly coupled to the electronic transition, provided the hole is burned near the flat maximum of the inhomogeneous site-distribution function. Figure 2 shows a correlation between ν_{ph} and the low-temperature elastic modulus of polymers E', obtained from ultrasonic measurements.[6] For several polymers (N6,6, PEMA, P*i*BuMA, P-1-B) E' from dynamic mechanical measurements[7] were used. Approximate linearity holds between the ν_{ph} and E' for the 13 polymers (exept PMP, POM and nylons 6, 11, 12): $\nu_{ph} = (-4.7\pm2.6) + (2.4\pm0.3)E'$, with correlation coefficient r=0.91. Similar correlation can be obtained for the dynamic shear modulus or the veloci-



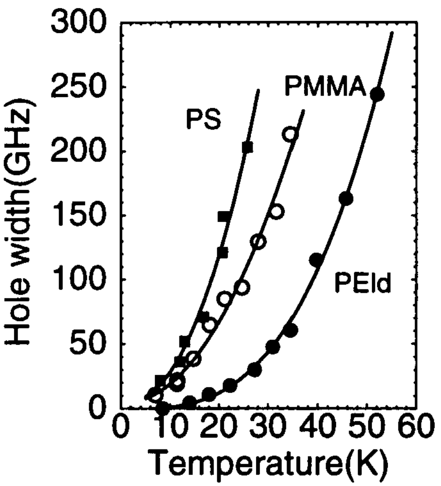


FIGURE 1 (left) Absorption change in the spectra of *t*-Bu-TAP in low-density PE and poly(4-methyl-1-pentene)(PMP) upon the exposure to the light dose of 50mJ/cm^2 at 619nm (PE) or 618nm (PMP) at 8K. The latter is up-shifted by 0.2 O.D. units.

FIGURE 3 (right) Temperature dependence of the quasihomogeneous hole widths in *t*-Bu-TAP/polymer systems. The power-law fits have coefficients 2.34(PS), 2.06(PMMA) and 3.11(low-density PE).

ties of longitudinal and transverse ultrasound waves.[6]

In Figure 3 the quasihomogeneous width(Γ_{qh}) of the holes in PS, PMMA and PE is plotted *vs* temperature. Γ_{qh} displays strong dependence on the host, ranging from 26GHz in polyethylene to 200GHz in polystyrene (at 25K) (Figure 4). In the temperature range under investigation the magnitude of kT is close to ν_{ph}. As a result, the thermal broadening of optical transitions is determined by quadratic interaction with the same low-frequency vibrations that make up the phonon wing.

Correlation between the elastic properties on one hand and ν_{ph} and Γ_{qh} on the other hand can be clearly followed in the series of polyolefines: PE, P-1-B, PP and PMP. PE is a "rigid" material (E'=10.3GPa), whereas PMP is very "soft" (E'=3.4GPa).[6] Acoustical and mechanical properties of low- and high-density PE are nearly identical.[6] The same is true for the Γ_{qh} values at 10K (~0.5 and ~1.3GHz) or at 25K (26±4 and 29±2GHz), for l.d. and h.d. PE, respectively. Γ_{qh} values in isotactic and atactic PP are the same within the accuracy of our measurements (10±2GHz at 10K and 80±10GHz at 25K).

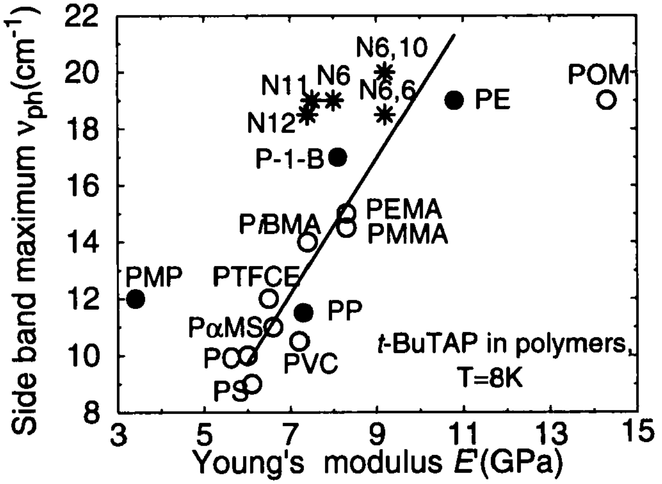


FIGURE 2 Relationship between the peak position of the phonon side band and the elastic modulus of the polymer host. Non-polar polymers (filled circles): PE polyethylene, PP polypropylene, P-1-B poly(1-butene), PMP poly(4-methyl-1-pentene); polar polymers (open circles): POM polyoxymethylene, PEMA poly(ethyl methacrylate), PMMA poly(methyl methacrylate), P*i*BMA poly(*iso*-butyl methacrylate), PTFCE poly(trifluoro chloroethylene), PαMS poly(α-methylstyrene), PVC poly(vinyl chloride), PC polycarbonate, PS polystyrene; H-bonded polymers (stars): N6,10 nylon 6,10, etc.

Inhomogeneous absorption contour in polyolefines is remarkably narrow: the half width at half maximum (HWHM) for the red side of the band at 8K equals to 95±10cm^{-1}. In other polymers the bands are much broader (HWHM=160±20cm^{-1}). The obvious reason for different inhomogeneous broadening consists in different local electric field variations in polar and non-polar media. Phonon-induced modulation of the internal field can be responsible for hole broadening as well. Thus the Γ_{qh} values of most of the polymers lie above the regression line of polyolefines (and polyamides).The polyoxymethylene (POM) is characterized by the highest elastic moduli.[6] Still the holes in POM are broader than in PE (52±3 and 26±4GHz at 25K, respectively). The hydrocarbon fragment in P*i*BuMA reduces the Γ_{qh} value in this matrix (90±10GHz at 25K). Rather narrow holes have been measured for porphine in polybutylacrylate.[2] A similar narrowing effect occurs in poly(vinyl butyral)(PVB) in comparison with PMMA.[9] It was emphasized that the flexible aliphatic group may facilitate the tight packing of polymer chains by

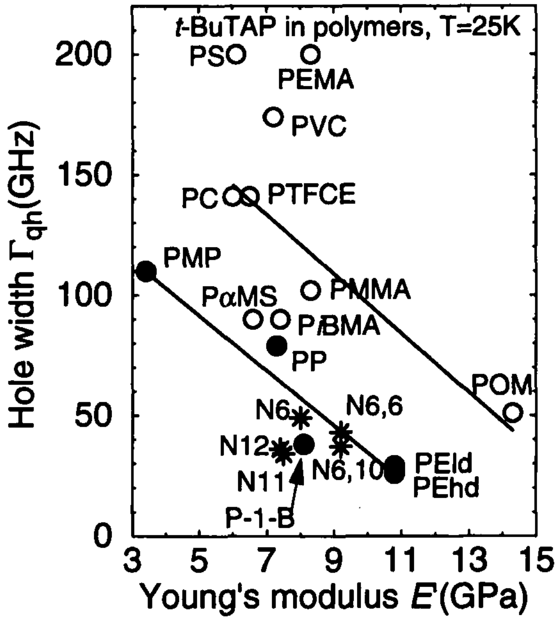


FIGURE 4 Relationship between the quasihomogeneous width of spectral holes at 25K and the elastic modulus of the polymer host, denoted as in Figure 1 .

leaving less voids in the matrix.[2] This in turn may reduce the degrees of freedom of certain atomic fragments which give rise to the tunneling systems. However, at higher temperatures *T*=8-50K negligible polarity of the side group seems to be of main importance. Large hole width in PS indicates that it should be regarded as a pseudopolar medium, because of the quadrupole moment or strong polarizability anisotropy of the benzene ring.

Excessive broadening in PEMA seems to be in contradiction with the previous arguments because the ethyl is a larger apolar substituent than methyl. The anomalous behavior of PEMA as compared to PMMA and P*i*BuMA becomes evident when we consider dynamic mechanical properties of these polymers (Figures 8-11 in ref 10). Between 5 and 40K the elastic modulus of PEMA drops from 8.3 to 7.5 GPa and, more importantly, the mechanical losses increase nearly by an order of magnitude due to the so-called δ-relaxation.[7,10] The α-methyl substitution in PS leads to a more noticeable hole narrowing, than expected solely on bases of the Young's modulus or the phonon frequency. Also, the δ-relaxation peak of mechanical losses in PS at ~40K disappeares in PαMS, presumably because of steric hindrance to phenyl motion by adjacent methyl group.[7]

Polyamides (nylons) possess both uniformly high value of ν_{ph}=18-20cm^{-1} and small Γ_{qh} which are relatively independent on *E*'. Macromolecular chains in nylons can be mutually cross-linked by hydrogen bonds between the amido fragments. This may lead to a considerable suppression of the local molecular dynamics.

CONCLUSIONS

Vibronic coupling to the low-frequency modes have been investigated by the method of spectral hole burning in a set of various polymers with known mechanical and acoustical properties at low temperatures.[6,7,10] Characteristic frequencies of most active vibrations lie between 9 and 20cm^{-1} and are in good correlation with the Young's modulus(*E*') and the shear modulus of the polymer. The strength of quadratic electron-phonon coupling also shows parellelism with the elastic characteristics of matrix. In saturated hydrocarbon polymers the density modulation may prevail as a line broadening mechanism. The local electric field modulation by acoustic waves provides an additional efficient hole broadening mechanism in polar polymers. The local molecular dynamics manifests itself in hole broadening in the polymers (PS, PEMA) displaying considerable mechanical losses (δ - relaxation) at low temperatures. The effect of the crystallinity and tacticity of the same polymer appears to be negligible between 8 and 50K.

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