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Charge Distribution in Halogenated Hydrocarbons and Intermolecular Interactions. A Way for Determining Compatibility in Polymer Blends

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CHARGE DISTRIBUTION IN HALOGENATED HYDROCARBONS AND INTERMOLECULAR INTERACTIONS. A WAY FOR DETERMINING COMPATIBILITY IN POLYMER BLENDS

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Abstract In the study of compatibility in polymer blends the importance of specific electrostatic interactions is generally acknowledged. What is generally needed are ways to evaluate the tendency of the components to form blends. The existence of positive or negative sites active in the blending process can be indicated by IR spectroscopy through the measure of absolute or relative infrared intensities. Ab initio calculations may be of great help when spectroscopic experimental data are not available.

1. INTRODUCTION

Polymer blends have a much larger versatility than their components: in fact, the macroscopic properties of a blend may be very different from those of the components. Thus, a great interest in basic and applied science of these materials has been developed.[1]

A polymer blend is a physical mixture of two or more polymers. The discussion of compatibility to form blends is still matter of active research.[1,2] However, there seems to be a general agreement on the fact that there is no compatibility between polymers **a** and **b** when they are not able to develop either weak or strong specific interactions.[1] The formation of a polymer blend seems to be due "to a balance between a free volume contribution (always unfavourable) and an interaction term (potentially favourable)".[2] The interaction term, in turn, is a balance between self-association (**a-a**, **b-b**) and hetero-association (**a-b**). Beside this, conformations are very important for compatibility.[2]

Much work has been done trying to predict whether polymers **a** and **b** are compatible prior to their formation of the **a-b** blend. The solubility parameter[3] δ_a and the infrared interaction parameter[4] χ_{ab} have been defined and are often used to predict compatibility. However, these parameters are the less reliable the stronger the specific interactions between **a** and **b**. Just in this case, IR spectroscopy may be of help.

The specific interactions between polymers **a** and **b** are essentially electrostatic[1]: dipole-dipole, dipole-induced dipole, hydrogen bond, charge transfer. Therefore, they are essentially due to the charge distribution in the molecules of components **a** and **b**. We have recently shown[5] that direct information on charge distribution can be obtained from infrared intensities. Indeed, from accurate intensity data, effective atomic charges and charge fluxes can be obtained. The knowledge of atomic charges allows calculation to very good approximation of the stabilization energy[6] of molecular complexes and should therefore be able to give the kind and extent of specific interaction in polymer blends also. When the absolute infrared intensities cannot be measured in an accurate way, the relative intensities can supply qualitative information on the charge distribution[7] and indicate trends in the possible interactions. This may be particularly useful in the case of polymers, where measurements of absolute intensities are practically impossible. Finally, when no experimental data from infrared intensities are available, information on the possible interactions can be derived from the atomic charges calculated by ab initio methods[8,9].

2. THE METHOD

The interaction energy between two molecules forming a molecular complex can be evaluated with a purely electrostatic model[6] by

$$\Delta E = \sum_{\alpha}^{N_a} \sum_{\beta}^{N_b} \frac{q\alpha\, q\beta}{r\alpha\beta}; \qquad (1)$$

$q\alpha$ and $q\beta$ are the effective atomic charges, N_a and N_b are the number of atoms in the molecules **a** and **b** respectively; $r\alpha\beta$ is the distance between atom α of molecule **a** and atom β of molecule **b**. Notice that, assuming the charge distribution to be perfectly described by atomic charges q, eq. 1 gives the best value of ΔE. Any expression using multipole interactions is, in this case, a lower approximation to eq. 1[10]. In the case of a polymer blend **a-b** one should evaluate the amount of charges $q\alpha$ and $q\beta$ for each polymer **a** and **b** or for smaller molecules containing the same group of atoms. We may do this three different ways:

2.1 From absolute infrared intensities

The infrared intensities of the band due to the i-th normal mode Q_i of a molecule is given

by

$$I_i = \text{const} \left| \frac{\partial \vec{M}}{\partial Q_i} \right|^2 \tag{2}$$

where $\vec{M}$ is the molecular dipole moment. Assuming that[5]

$$\vec{M} = \sum_{\alpha} q_\alpha \vec{r_\alpha} \tag{3}$$

one has $\frac{\partial \vec{M}}{\partial Q_i} = f(q_\alpha, \frac{\partial q_\alpha}{\partial Q_i})$ where q_α are the so-called atomic charges. The knowledge of all the I_i of the molecule permits evaluation of q_α.

As an example we report in figure 1 the results of a study of infrared intensities of CH_3OH, $(CH_3)O(CH_3)$ and of $(CH_3)_2C=O$. We will see later how the differences of atomic charge on the oxygen atom of the three molecules can be helpful in predicting trends in the intermolecular interactions. Notice that q_H is very sensitive to the local electronic environment and molecular structure. It has been seen[5,7] that, while q_H is $\cong$0.04e in saturated n-alkanes, its value decreases to 0.02e for C-H groups trans to the lone pairs of oxygen atoms because of backdonation[7,11], increases to 0.07e for inductive effect when the C–H group is adjacent to an oxygen atom and to 0.12e when the hydrogen atom is part of a CH_3 hyperconjugated with a C=O group; q_H reaches very large positive values when, as in the case of methanol, hydrogen is bonded to an electronegative atom[6]. The different values of q_H can be used for prediction of the possibility of making bonds[6] with another molecule carrying a negative site. This classification would make, for instance, the "acidic" hydrogen atom of CH_3OH the most important and the backdonated hydrogen atoms the least important for the formation of molecular complexes with CH_3OH.

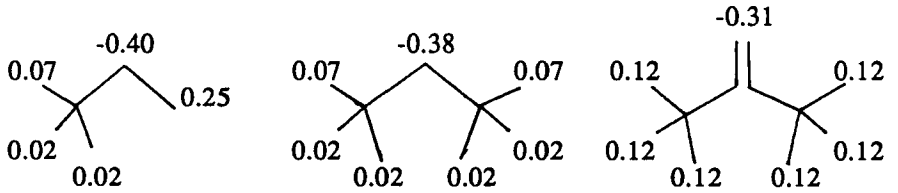


FIGURE 1 Atomic charges, q_α ,derived from infrared intensities for methanol, dimethylether and acetone. Units are electrons.

2.2 From ab initio calculations

The atomic charges can also be derived from "ab initio" calculations. It has been shown[8,9] that the so-called Mulliken charges[12] ζ_α^M describe the charge distribution in a way very similar to that obtained from infrared intensities. The agreement between q_α derived from experimental infrared intensities and ζ_α^M calculated with "ab initio" methods improves with the extension of the basis set[8,9]. However, even with a minimal basis set the trends suggested by infrared charges are respected.

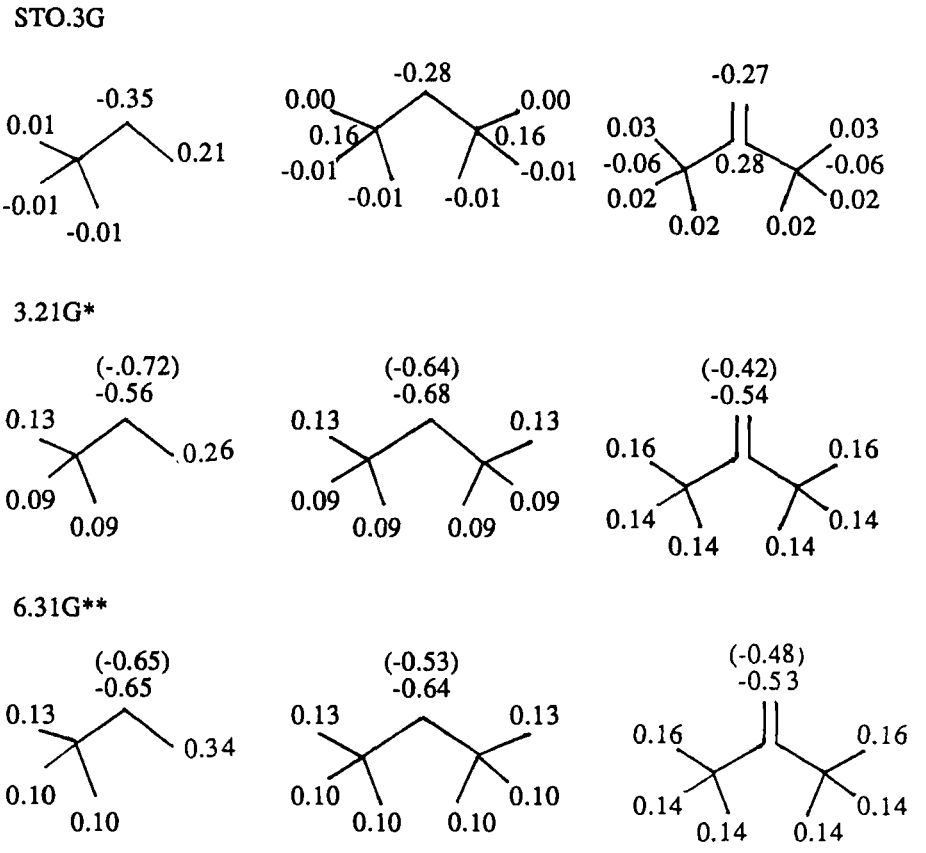


FIGURE 2 Atomic charges ζ_α calculated for methanol, dimethylether and acetone by "ab initio" methods at three different levels. The GAUSSIAN 82 calculation program has been used[13]. Values in parentheses are ζ_O^{CORR} (see text). Units are electrons.

In figure 2 we have reported the Mulliken atomic charges ζ_α^M obtained, according to their standard definition[12] with different basis sets. It can be noticed that the general

agreement between ζ_α^M (fig.2) and q_α (fig.1) is respected even at the STO.3G level and that it improves with the extension of the set. Recently, however, we have proposed[9] a correction to ζ_α^M obtained by forcing with respect to the calculated molecular dipole moment. The ζ_α^{CORR} can be computed by any "ab initio" program, at any level, and provide an even better agreement with the q_α than that shown by ζ_α^M. We have reported in fig.2 also the values of ζ_O^{CORR}, because, as commented on in the next section, the correction for electronegative atoms is not negligible.

2.3 From correlations of IR spectra

When the atomic charges are not available, either from IR intensities or from ab initio calculations, some simple correlations among values of peak frequencies and of relative intensities may suggest the correct trend in the classification of interactions. So far we are able to give convincing support to this statement only for what affects charges on hydrogen atoms bonded to carbon atoms. However, this is just what is important in the case of polymer blends where the positive active site is often an hydrogen atom bonded to a carbon atom. Our correlations rest on two experimental findings:

i) when the atomic charge q_H increases, the frequency of the C-H stretching, ν_{CH}, increases.

ii) when the atomic charge q_H increases, the ratio I^{def}/I^{str} between the intensity of the bands due to deformation modes and that of the ν_{CH} bands increases.

Full details on these findings have been reported elsewhere[7], together with the interpretation of this trend. Since we want to describe here only a possible application, a few details are sufficient. As for i), the frequency ν_{CH} should be that of the isolated CH and may be obtained by selective deuteration of all but one of the hydrogen atoms. The procedure has been introduced by Mc Kean[14] for correlation of ν_{CH} with interatomic distances r_{CH}. Some examples of the trend of q_H/ν_{CH} are reported in table 1. The same trends are observed by the charges and the frequencies within each family of molecules. Also the values of ζ_H^M (calculated at the 4.31G level) follow the same trend even if the absolute values are too large when compared with the experimental ones. A more extended basis set could give much better results, as shown in figure 2, but calculations become too expensive. In any case, when we do not know q_H from infrared, we may use ζ_H^M, provided that we compare only with other ζ_H^M calculated with the same set. We may even infer the relative value of q_H or ζ_H^M from ν_{CH}.

TABLE I Infrared charges (q_H), ab-initio Mulliken charges (ζ_H^M) and C-H stretching frequencies for some families of molecules

	q_H	ζ_H^M 6.31G**	ζ_H^M 4.31G	ν_{CH}
Ethane	.045	.112	.150	2950
Propane	.045	.105-.110	.146-.149	2920–2950
Butane	.045		.146-.149	2907–2949
Ethylene	.134	.127	.164	3060
Acetylene	.208	.235	.299	3336
Ethylene	.134	.127	.164	3060
Formaldehyde	.097	.099	.154	2813
Acetaldehyde	.038	.098		2770
Methane	.065	.118	.152	2992
Methanol t	.020	.099		2920
Methanol g	.070	.128		2979
Dimethylether t	.020	.10		2884
Dimethylether g	.070	.13		2984

As for item ii), let us stress the extreme convenience of this procedure. When all the CH are "equivalent", I^{str} is the infrared intensity of the whole region around 3000 cm^{-1} and, if no electronegative substituent is present in the molecule, I^{def} is the infrared intensity of the whole region from 1500 cm^{-1} downwards. Their ratio I^{def}/I^{str} is very easy to obtain with computerized instruments. When the CH are not equivalent from the electrical viewpoint, the value of the corresponding ν_{CH} may be different and the bands must be at least roughly separated. The behaviour of I^{def}/I^{str} versus q_H is very regular for molecules where no electronegative substituents occur (figure 3).We will see how the same trend can also be used in halogenated compounds. In conclusion, the correlations presented in this section allow looking at the infrared spectrum with new eyes. The variation of charge distribution within a family of molecules can often be estimated by simply looking at the relative value of ν_{CH} or at the relative intensities I^{def}/I^{str}. As a simple example we report, in table 2, some data for polyethylene, where the atomic charge is low, and for polyacetylene, where the atomic charge is much larger. Accordingly, the region spanned by ν_{CH} is at higher frequency for PA than for PE and the ratio I^{def}/I^{str} is much larger in PA than in PE.

TABLE II Comparison of infrared data for two typical hydrocarbons: polyethylene (PE) and polyacetylene (PA). q_H is from infrared intensities, ν_{CH} is the region where CH stretching occurs and I^{def}/I^{str} is the ratio between intensity of the region 1500-0 cm^{-1} and that of the region 3100-2800 cm^{-1}

	q_H	ν_{CH}	I^{def}/I^{str}
PE	0.045	2850-2950	0.11
PA	0.134	3000-3050	2.69

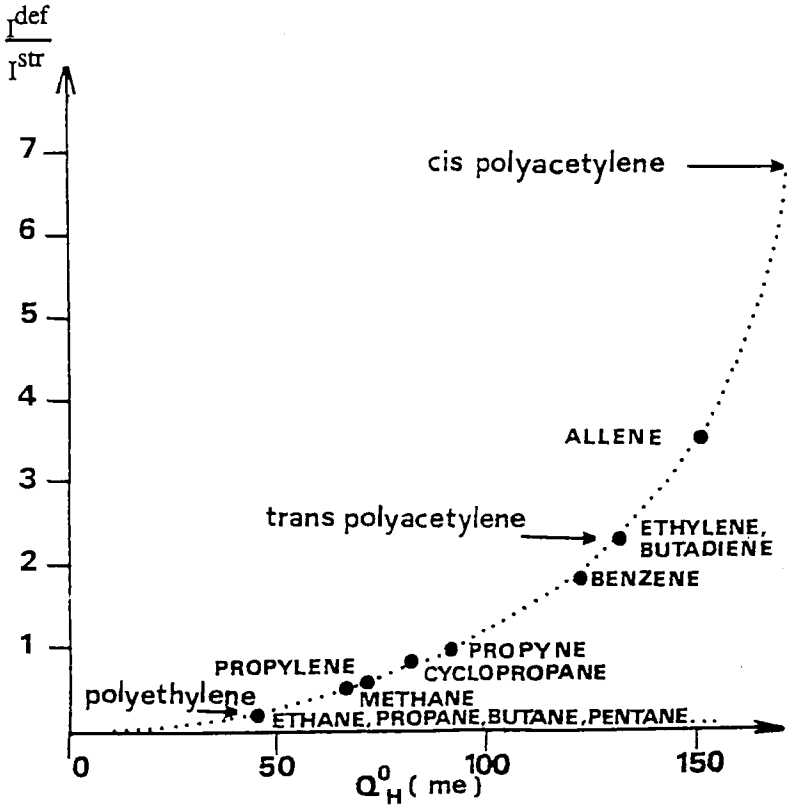
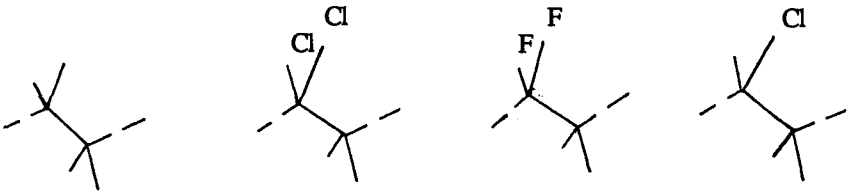


FIGURE 3 $I^{def}_{CH} / I^{str}_{CH}$ versus q_H for a number of hydrocarbons

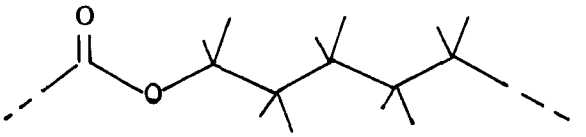
3. APPLICATION TO SPECIFIC INTERACTIONS IN POLYMERS

Let us consider polyethylene (PE) and some most common halogenated polymers:



PE PVDC PVDF PVC

Polyvinylidenchloride (PVDC), polyvinylidenfluoride (PVDF) and polyvinylchloride (PVC) are known to give compatible blends with many other polymers[2] as, for instance, poly-E-caprolactone (PCL):



The extent of some kind of specific interactions between PVDC, PVDF, PVC and PCL would traditionally be assessed[1,2] by looking at the shift of the $\nu_{C=O}$ in PCL after the formation of the blend. This procedure relies on minimal shifts ($\Delta\nu$ is less than 10 cm^{-1}) and does not have a predictive value before blending. Let us apply our approach and let us examine carefully the infrared spectra of these polymers (figure 4). The spectrum of PE is clearly dominated by the ν_{CH} bands (as always in saturated hydrocarbons) since the atomic charges q_H are very small. In PVDC and PVDF, on the contrary, the ν_{CH} bands are weak, as the q_H of CH_2 are large because of the induction by the two chlorine and the two fluorine atoms respectively. In the spectrum of PVC the situation is intermediate. The ν_{CH} bands are reasonably strong and are due to the CH_2 group, where q_H is certainly smaller than in PVDC because the content of Cl is less than in PVDC. The band ν_{CH_α}, due to the hydrogen atom which is in α position with respect to chlorine, is expected to have extremely small intensity (due to the fact that q_H is large) and must be assigned to a small shoulder around 3000 cm^{-1}.

The values of the ν_{CH} frequencies in the spectra of figure 4 are very interesting and worth mentioning. The observed ν_{CH} of the polymers are shifted from those observed for the isolated C-H groups in selectively deuterated molecules. A trend can still be observed, namely: $\nu_{CH}(PE) < \nu_{CH}(PVDC) < \nu_{CH}(PVDF)$.

As for PVC, the region spanned by ν_{CH} is approximately the same as in PVDC. Indeed what we see is ν_{CH} due to CH_2, more intense than in PVDC because the charge is a little smaller. The frequency of C-H_α appears as a small shoulder at ≈3000 cm^{-1}, with very weak intensity because q_{H_α} is rather large.

The ratio I^{def}/I^{str} is evidently increasing from PE to PVC, as expected. Because of the overlapping of some deformation bands with the bands due to Fluorine or Chlorine, it is better to compare, in the four spectra, the bands due to CH_2 bending in PE, PVDC, PVDF and to CH bending in PVC, as marked in Fig.4. Another interesting feature of these spectra is the variation in the intensity of the C-C stretching bands. C–C stretching is silent in PE for symmetry reasons (also the intrinsic value would be very low[15]) but is rather intense in halogenated polymers (1070 and 1040 cm^{-1} in PVDC; 1070 and 880 cm^{-1} in PVDF; 1100, 970 and 880 cm^{-1} in PVC). This is due to the strong polarization of the CC bonds induced by the electron attraction exerted by the halogen atoms on the hydrogen atoms in β position.

From the above simple observations on the four spectra we may suggest a classification of the four polymers with respect to possible specific interactions with another polymer containing a strongly negative group (such as C=O in PCL). The classification is, of course,

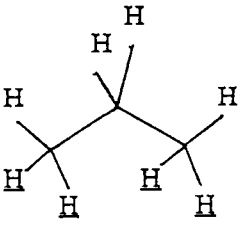
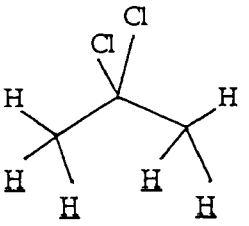
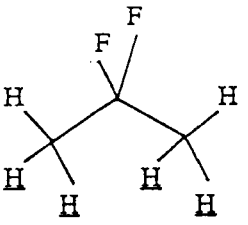
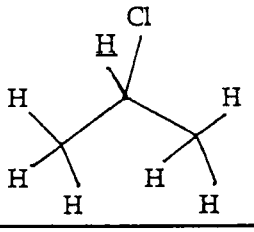
$$\left|\Delta E(PE)\right| < \left|\Delta E(PVDC)\right| < \left|\Delta E(PVDF)\right| < \left|\Delta E(PVC)\right| \qquad (4)$$

Notice that this classification can be made on the components of a possible blend without resorting to the blend itself. Other spectroscopic techniques, such as those that measure the shift of the ν(C=O) of carbonyl groups involved in blends, require the registration of the spectrum of the blend.

Quantitative support of this classification can be given by the use of some data from small molecules containing hydrogen atoms with an electrical situation similar to that of the above polymers. We may assume that: i) in the CH_3 of propane the hydrogen atoms trans to CH_2 are similar to those of PE; ii) in the CH_3 of 2-dichloropropane (2-difluoropropane) the hydrogen atoms trans to CCl_2 (CF_2) are similar to those of PVDC (PVDF); iii) the hydrogen atom in CHCl of 2-chloro-propane is similar to the H_α in PVC. We have reported in table 3 the ζ_H^M calculated by 4.31G ab initio methods and the ν_{CH} frequencies measured by Mc Kean[14] with the selective deuteration method. The values reported in table 3 confirm the classification (4).

Among the polymers considered in this work, PVC is the one most generally known as capable to form compatible blends with many other polymers. We think that a possible explanation for this compatibility is the large q_H value of the hydrogen atoms α to the chlorine. A recent study[16] of PVC/PCL blends indicates the α-hydrogen as responsible

TABLE III Calculated atomic charges (4.31G) and observed CH stretching frequencies for model molecules of PE, PVDC, PVDF, PVC. The values refer to H in each molecule.

	ζ_H (4.31G)	$\nu_{CH}^{isolated\ 14}$
	.15	2950
	.18	2988
	.18	3010
	.22	3025

for the specific interaction in PVC blends. This conclusion has been reached by showing that, in PVC/PCL blends, the ν_{CCl} does not shift while the ν_{CD} of α-deuterated samples of PVC does shift. Prior to this study, it was believed that the interaction PVC/PCL could be described mainly by a dipole-dipole term involving C=O (PCL) and C-Cl (PVC). Reference (16) gives many reasons against this description. We add that the leading term in ΔE would be $\vec{\mu}(C{=}O)\cdot\vec{\mu}(C\text{-}Cl)$ only for the case that $|\vec{\mu}(C\text{-}Cl)| >> |\vec{\mu}(C\text{-}H)|$. The

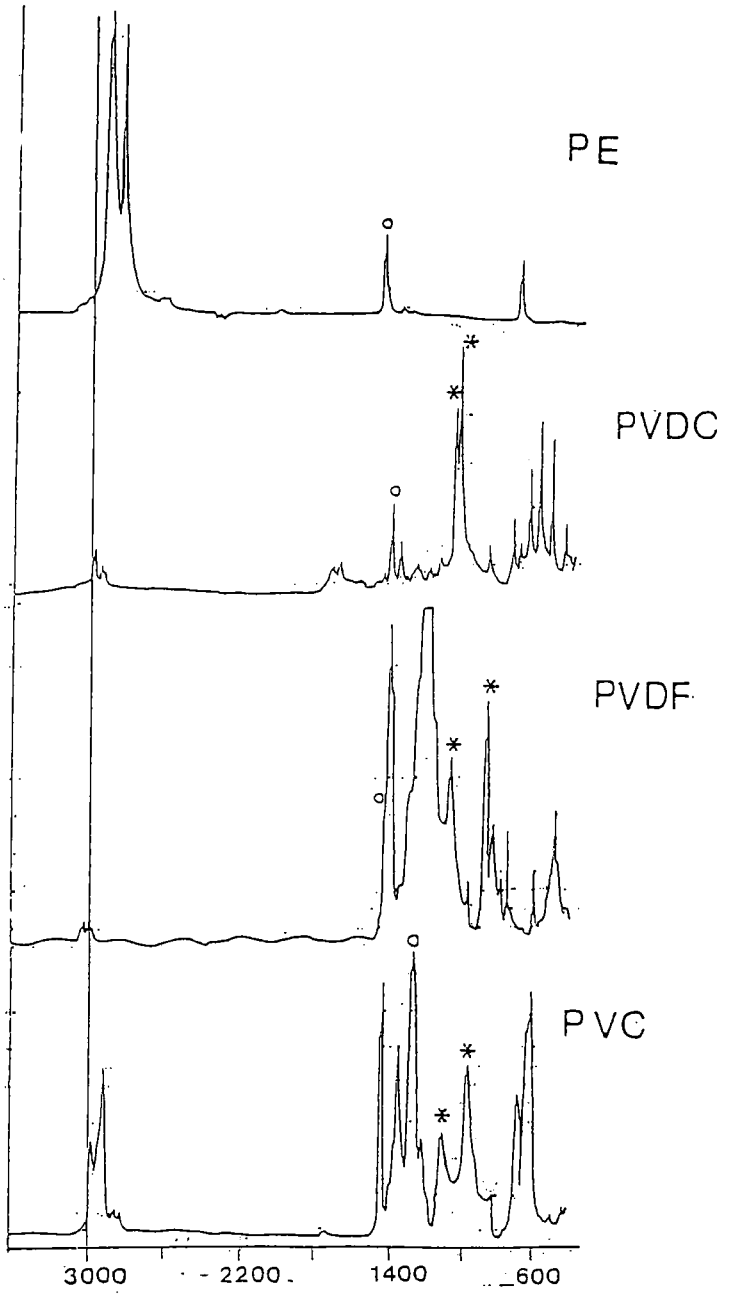


FIGURE 4 Infrared spectra of polyethylene (PE), polyvinylidenchloride (PVDC), polyvinyliden-fluoride (PVDF) and polyvinylchloride (PVC). ° : CH_2 or CH bending; * : CC stretching

idea that $|\vec{\mu}(C\text{-}X)|$ (X=halogen) be much larger than $|\vec{\mu}(C\text{-}H)|$ has been often proposed in the past and is based on the comparison between Mulliken's charges ζ_X^M and ζ_H^M; this comparison gives $|\zeta_X^M| >> |\zeta_H^M|$. However, we know now that the Mulliken charges of strongly electronegative atoms are strongly affected by not having considered atomic dipoles and lone pairs[9]. In a paper[17] discussing the above quoted correction to Mulliken charges, we have recently shown that, while the correction to ζ_H^M is never very large, the correction to ζ_X^M is large, so that $|\zeta_X^{CORR}| \cong |\zeta_H^{CORR}|$. Therefore, while ζ_X^M would suggest $|\vec{\mu}_{C\text{-}X}| >> |\vec{\mu}_{C\text{-}H}|$, ζ_X^{CORR} indicates that $|\vec{\mu}_{C\text{-}X}| \cong |\vec{\mu}_{C\text{-}H}|$. Let us stress that the difference between ζ_α^M and ζ_α^{CORR} is large mainly for α = electronegative atom but they are not so large in the case of hydrogen.

In conclusion, we want to consider some blends for which trends in atomic charge of the components may be useful for judging compatibility. Let us consider for instance the experimental finding[2] that blends between PCL and polyvinylphenol (PVPh) show hetero-association (PCL-PVPh) smaller than self-association (PVPh-PVPh). This fact can be rationalized in terms of charge considering that in both cases the positive element of the interaction is the acidic hydrogen of O-H in PVPh while the negative atom is oxygen of the carbonyl group in PCL and oxygen of the hydroxyl group in PVPh. Since both q_O and ζ_O^M (figure 1,2) indicate that

$$|\text{charge of carbonyl oxygen}| < |\text{charge of hydroxyl oxygen}|,$$

the above experimental finding could be predicted. In a similar way, it can be predicted that, in blends with poly-β-propiolactone (PPL), it happens that

$$|\Delta E(PPL/PVC)| < |\Delta E(PPL/PVPh)|$$

because the negative element is the same (oxygen of the carbonyl group) while the positive element is H_α in PVC and $H_{O\text{-}H}$ in PVPh.

All the examples quoted above seem to support the approach we present in this paper for predicting and/or understanding compatibility in polymer blends. While we have considered in this work only the role played by specific pairwise electrostatic interactions through atomic charges, we may have neglected other important contributions such as the conformational flexibility.

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