cal displacement related to the change of λ_1 and λ_2 is 1.05%, the average value obtained from the experiment is (1.05 ± 0.03)%. There is good agreement between the experimental and theoretical displacements and orientation values.

The polychromatic illumination can be considered as made up of a discrete number of constituent wavelengths, each individually capable of producing a coherent speckle pattern. A reduced speckle, the one due to all wavelengths acting together, can be regarded as the incoherent addition of a number of coherent speckle patterns each displaced according to the individual wavelength, with the resulting effect of 'smoothing' of polychromatic speckle patterns[7].

The speckle produced by SALS may also be reduced by employing the method of time integration while the wavelength is fixed. Trivial yet important with respect to its consequences is the finding that in many cases such integration (analogous to the use of the random spatial phase modulator[8]) may be realized by motion of the scattering medium alone. This has been experimentally verified for light scattering from dispersions[9] (low-speed stirring of the sample). A similar procedure (rotation of the sample) may be employed also for unoriented solid polymers. The speckle noise in this case is reduced because of total averaging out of the interparticle interference function over the different particle configurations of the scattering units during the counting time or time of exposure.

The new findings reported here concern the spectral correlation of speckle created by SALS and point out the importance of investigation of the detailed properties of speckle with an aim to utilize the speckle analysis in the characterization of the medium by which it is created[3–5].

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Solubility parameters of ternary solvent mixtures; calculation of the solvent composition with maximum polymer interaction

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Rigbi[1] has applied vector algebra to the calculation of the composition of binary or ternary solvent mixtures, leading to a maximum in the interaction with a given polymer in terms of the three-dimensional solubility parameter as proposed by Hansen[2] and applied by us to binary solvent mixtures[3]. The equations as given by Rigbi for each of the solubility parameter components in a ternary mixture appear not to be in accord with the requirement of symmetry with regard to the three component solvents (equation 8 in ref 1). Here, we give a more concise and mathematically more satisfying derivation of the optimum composition of ternary solvent mixtures.

As in Rigbi's paper the three-dimensional solubility parameters are represented by vectors; the three solvents are symbolized by $\underline{a}$, $\underline{b}$ and $\underline{c}$, the polymer by $\underline{p}$ and the optimum solvent mixture by $\underline{m}$. The end points of the respective vectors in the solubility parameter space are A, B, C, P and M. The requirement for maximum interaction is that PM is perpendicular to the plane through A, B and C; in other words PM $\perp$ AB and PM $\perp$ AC. In vector notation:

$$(\underline{m}-\underline{p})^{\mathrm{T}}(\underline{b}-\underline{a})=0 \tag{1}$$

$$(\underline{m}-\underline{p})^{\mathrm{T}}(\underline{c}-\underline{a})=0 \tag{2}$$

M lies in the ABC plane, from which follows that $(\underline{m}-\underline{a})$ is a linear combination of $(\underline{b}-\underline{a})$ and $(\underline{c}-\underline{a})$:

$$(\underline{m}-\underline{a})=\lambda_1(\underline{b}-\underline{a})+\lambda_2(\underline{c}-\underline{a}) \tag{3}$$

Elimination of $\underline{m}$ by substitution of equation (3) into equations (1) and (2) gives a set of two linear equations for λ_1 and λ_2:

$$\begin{aligned}(\underline{b}-\underline{a})^{\mathrm{T}}(\underline{b}-\underline{a})\lambda_1+(\underline{c}-\underline{a})^{\mathrm{T}}(\underline{b}-\underline{a})\lambda_2&=(\underline{p}-\underline{a})^{\mathrm{T}}(\underline{b}-\underline{a})\\(\underline{b}-\underline{a})^{\mathrm{T}}(\underline{c}-\underline{a})\lambda_1+(\underline{c}-\underline{a})^{\mathrm{T}}(\underline{c}-\underline{a})\lambda_2&=(\underline{p}-\underline{a})^{\mathrm{T}}(\underline{c}-\underline{a})\end{aligned} \tag{4}$$

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Table 1 Calculated polymer/solvent mixture interactions

	Solubility parameters[a] ($J^{1/2}$ $cm^{-3/2}$)			Optimum volume fractions		Δ^b ($J^{1/2}$ $cm^{-3/2}$)	
Mixture	δ_d	δ_p	δ_h	Ref 1	This paper	Ref 1	This paper
1 Polybutadiene	17.00	0	1.02				
Toluene	18.05	1.4	2.0	−0.123	0.993		
Hexane	14.78	0	0	1.068	0.311	0.522	0.448
Chlorobenzene	19.00	4.3	2.0	0.055	−0.304		
2 Poly(acrylonitrile)	18.24	16.17	6.75				
DMF	17.44	13.7	11.2	1.218	0.336		
Nitromethane	15.76	18.8	5.1	0.024	0.574	2.849	1.674
Chlorobenzene	19.00	4.3	2.0	−0.242	0.090		
3 Nylon-6,6	18.54	5.12	12.28				
n-Propanol	14.90	6.7	17.4	0.040	0.524		
Water	12.28	81.3	34.2	0.072	0.002	1.760	2.266
Trichloroethylene	17.97	3.1	5.3	0.888	0.474		
4 Poly(vinyl chloride)	18.73	10.0	3.1				
Chloroform	17.70	3.1	5.7	0.075	0.674		
THF	16.82	5.7	8.0	3.400	1.230	0.426	6.600
Butyl acetate	15.70	3.9	6.3	−2.475	−0.904		
5 Poly(ethylene terephtalate)	19.52	3.5	8.6				
Chlorobenzene	19.00	4.3	2.0	0.125	−1.700		
Toluene	18.05	1.4	2.0	0.441	1.532	4.366	4.732
Cyclohexanone	17.70	8.4	5.1	0.434	1.168		

[a] Values from ref 1

[b] Distance of polymer to optimum mixture in δ space

from which λ_1 and λ_2 may be found.

Substitution of λ_1 and λ_2 in the three equations (3) gives:

$$m_1 = (1-\lambda_1-\lambda_2)a_1 + \lambda_1 b_1 + \lambda_3 c_1$$

$$m_2 = (1-\lambda_1-\lambda_2)a_2 + \lambda_1 b_2 + \lambda_2 c_2 \qquad (5)$$

$$m_3 = (1-\lambda_1-\lambda_2)a_3 + \lambda_1 b_3 + \lambda_2 c_3$$

where m_1, a_1 etc. are the components of the solubility parameter vectors. The coefficients in equation (5) are equal to the volume fractions of the solvent a, b and c in the optimum mixture.

In Rigbi's paper[1] the equations (5) are given as:

$$m_1 = \varphi_a a_1 + (\varphi_b + \varphi_c)(\varphi_b b_1 + \varphi_c c_1) \text{etc.}$$

The coefficients in these equations are not cyclically interchangeable. The results calculated for φ (by means of numerical solution) are therefore not satisfactory, whereas our equation (5) is derived directly from the model.

We have recalculated some of the mixtures given in ref 1*; the results are given in *Table 1*. As noted by Rigbi, negative volume fractions and volume fractions larger than 1 are found in several cases; this simply means that the solvent power of the ternary mixture is less than that of a binary mixture or a single solvent.

From the results it can be concluded that the calculated compositions of the solvent mixtures which give a maximum interaction with the polymers differ from those given by Rigbi[1]. The conclusions drawn by this author on the role of non-solvents in some of the cases studied are therefore questionable.

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* Calculations were performed on a HP 9830 A calculator; copies of the HP BASIC program are available on request.