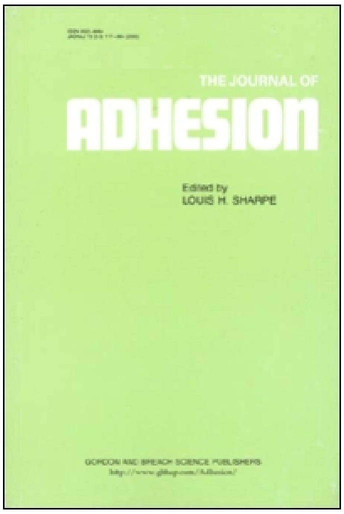

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E. P. Chang[a]; Daniel Holguin[b]
[a] Avery Research Center, Pasadena, California, USA [b] Avery Dennison Performance Polymers, Pasadena, California, USA

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Electrooptical Light-Management Material: Low-Refractive-Index Adhesives

E. P. Chang
Avery Research Center, Pasadena, California, USA

Daniel Holguin
Avery Dennison Performance Polymers, Pasadena, California, USA

A prototype pressure-sensitive adhesive that has a low refractive index (< 1.36) and is optically clear has been developed (Holguin and Chang, US Patent 6703463, 2002). The refractive index is a key feature in the application of optical polymers, and this pressure-sensitive adhesive is particularly useful for light-transmitting devices. It is a fluoro-substituted mono-acrylate adhesive. Fluoro-polymers are known to have a low refractive index, but typically the fluoro-polymers are not sticky and are opaque because of their crystallinity. The design of this novel fluorosubstituted monoacrylate adhesive polymer is based on the rheological marriage of fluoro-polymers and pressure-sensitive adhesives.

Keywords: Electrooptics; Fluorinated acrylics; Light-management materials; Low refractive index; Low surface energy; Nonhalogenated solvent; Pressure-sensitive adhesive

INTRODUCTION

The objective is to develop optical adhesives useful in light-transmitting devices that help control light distribution (*i.e.*, antiglare, anti-iridescence, low reflectance, and low interference products). This is achieved by employing adhesive polymers with a low refractive index (<1.36) to obtain the desired light distribution. The objective of this article is to develop pressure-sensitive adhesive (PSA) polymers with the desired physical properties of refractive index, glass transition temperature (T_g), light transmittance, and adhesion.

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Address correspondence to Eng Pi Chang, Avery Dennison Research Center, 2900 Bradley Street, Pasadena, CA 91107-1599, USA. E-mail: pi.chang@averydennison.com

An example of an application [1] where a low-refractive-index adhesive can obtain the desired light distribution is a rear projection screen for a television (back-lit projection screen). The Fresnel collimating lens for use with a projection screen should maintain the capability of effectively collimating light to provide uniform brightness across the screen. It is generally advantageous to increase the difference between refractive indices of the Fresnel lens and other components to help control light distribution (Figure 1). This can be achieved by using a low-refractive-index adhesive to attach the secondary component to the Fresnel lens. The Fresnel lens material is glass or poly(methylmethacrylate) with a refractive index of 1.53 and approximately 1.49, respectively.

Noting the refractive index of the Fresnel lens material, a significant difference would be a refractive index of less than 1.4. Only air, water, and fluoro-polymers have refractive indices of less than 1.4.

Currently, for applications where there is a significant distance between the components of the light-transmitting devices, light source, lens (or lenses), and other components, the medium is air and the components are mechanically supported. Air is a poor supporting medium.

There is one light-receiving device that uses water as a medium—the eye. The eye actually uses a natural hydrogel as the medium and has a refractive index of 1.336 (Figure 2).

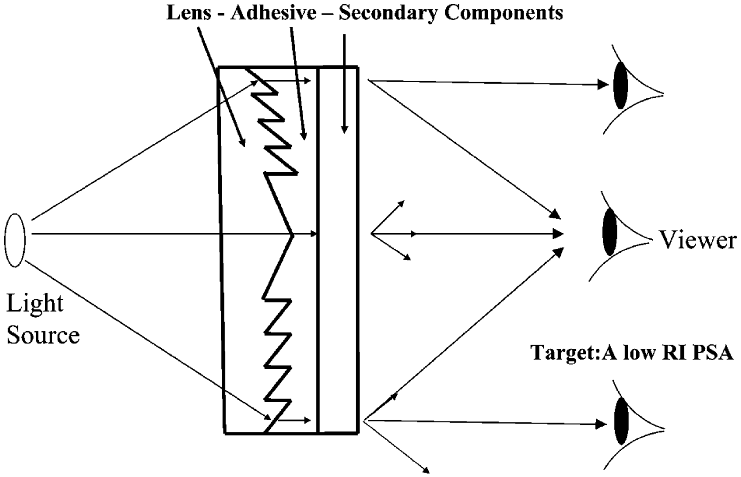


FIGURE 1 Typical component setup of a rear projection screen.

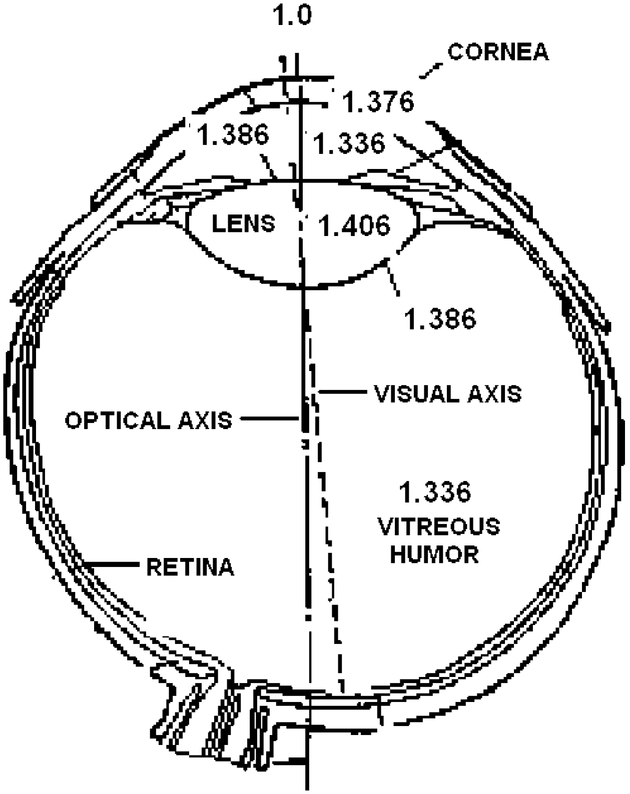


FIGURE 2 Refractive index of the different components of the human eye.

Low-Refractive-Index Hydrogels

We investigated and developed hydrogels as a low-refractive medium [2]. Figure 3 shows the use of ultraviolet (UV)-curable water-soluble oligomers for making hydrogels. Water is very effective in making a low-refractive-index medium, but to get below 1.36 the hydrogel would have to contain more than 80% water. This is a very cost-effective product but not a likely candidate for a long-term PSA.

Refractive Index of Fluoro-polymers

Figure 4 shows the correlation of refractive index with the percentage of fluorine in the polymer. The higher the percentage of fluorine, the lower the refractive index. To achieve a polymer with refractive index of <1.36, the percentage of fluorine content has to be >57%.

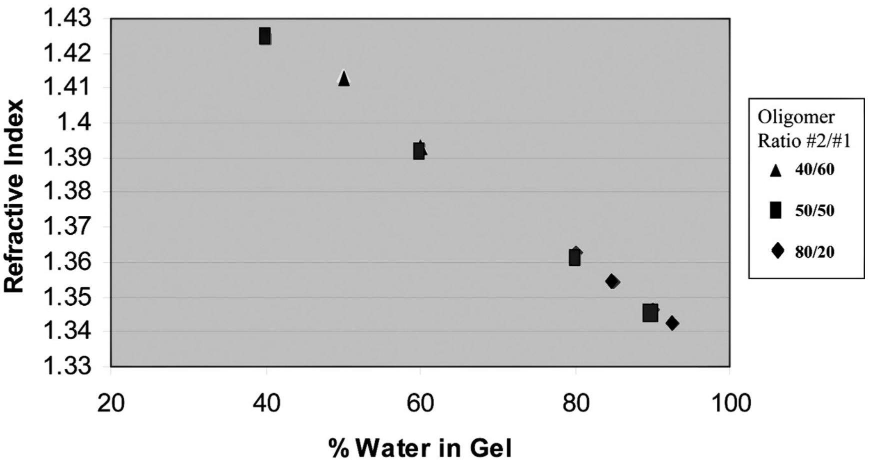


FIGURE 3 Refractive index of UV-cured hydrogels as a function of % water.

Lorentz–Lorenz Equation and Correlation Model of Groh and Zimmerman

The relationship between refractive index with molar refraction and molar volume is shown in the Lorentz–Lorenz equation [3, 4]:

$$(n_{\mathrm{D}}^2 - 1) * M_{\mathrm{G}} = R_{\mathrm{L}} \qquad (1)$$

$$(n_{\mathrm{D}}^2 + 2) * \rho$$

where n_{D} is the refractive index, M_{G} is the repeating unit molecular weight, ρ is the density, and R_{L} is the molar refraction.

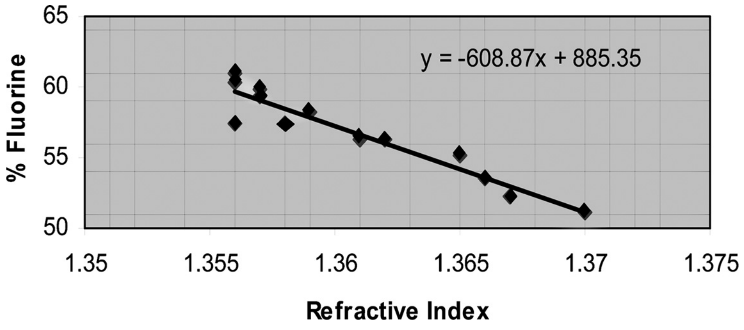


FIGURE 4 Correlation of experimental refractive index with % fluorine.

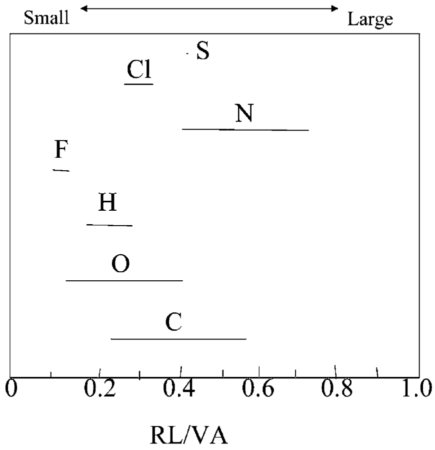


FIGURE 5 Variation of molar refraction to molar volume ratio with different atoms.

It can be observed from Equation (1) that a low refractive index can be achieved by either lowering the molar refraction or increasing the molar volume.

Groh and Zimmerman plotted the ratio of molar refraction, R_L, to molar volume, V_L, for different atoms present in organic polymers [5] using previously published data [6–8]. In spite of the broad range of values for each atom because of their different binding structures and varying chemical environments, it is apparent that fluorine, and to a lesser extent oxygen, lowers the refractive index of a compound as shown in Figure 5.

EXPERIMENTAL

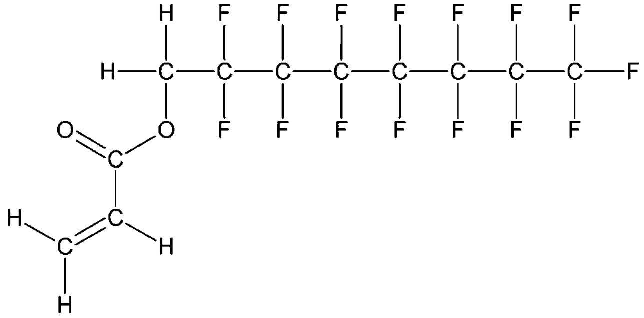
Materials

Based on this concept, as well as the material-property requirements of PSAs, the preferred molecular structure to investigate was fluorination on the bulky polymer side chain (*i.e.*, to increase the molar volume and to decrease the molar refraction by fluorination) rather than the more typical fluorinated-polymer main chain [*e.g.*, poly-(tetrafluoroethylene) which is hard and crystalline]. Also, a fluoro-polymer with the side chain fluorinated was needed for the polymer to be soluble in a nonhalogenated solvent for processing.

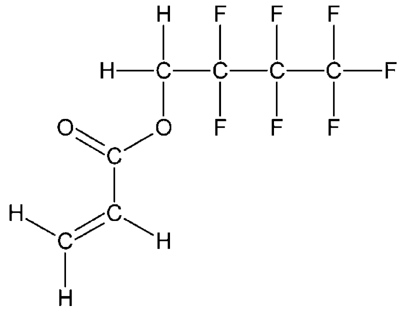
The side chain fluoro-acrylate monomers used in this work were selected based on commercial significance (cited on the Environmental

Protection Agency TSCA Inventory list): PDFA = 1H,1H-pentadecafluorooctyl acrylate (Synquest Laboratories, Alachua, FL, USA) and HFBA = 1H,1H-heptafluorobutyl acrylate (Synquest Laboratories). A nonfluorinated comonomer, AA = acrylic acid (Sigma-Aldrich, Milwaukee, WI, USA), was used for organic solvent solubility, ionic cross-linking, and as a specific adhesion promoter. See Schemes 1–3.

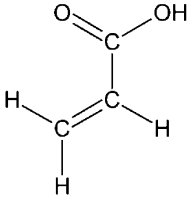
A typical polymerization [1] reaction is as follows: Ethyl acetate solvent (20 g) was added into a 100-ml reactor equipped with a nitrogen purge, an agitator, and a reflux condenser. The solvent was heated to reflux with a jacket at 85°C. A monomer mixture of 44.0 g PDFA, 24.0 g of HFBA, 1.0 g of AA, and 0.084 g of 2,2′-azobis(2-methylbutyronitrile) (a polymerization initiator commercially available as Vazo 67® from E. I. DuPont de Nemours, Wilmington, DE, USA) was slowly added to the reactor over a period of 2 h. After the reactor contents were allowed to react for 1 h, 1.7 g of ethyl acetate and 0.05 g of Vazo 67 were added to the reactor. The reactor contents were allowed to



SCHEME 1 1H,1H-pentadecafluorooctyl acrylate (PDFA).



SCHEME 2 1H,1H-heptafluorobutyl acrylate (HFBA).



SCHEME 3 Acrylic acid (AA).

further react for 1 h before a second portion of 1.7 g of ethyl acetate and 0.05 g of Vazo 67 initiator were added to the reactor. An additional 1.7 g of ethyl acetate and 0.05 g of Vazo 67 initiator were added to the reactor after the reactor contents were again permitted to react for 1 h. After the addition of the third portion of initiator, the reactor contents were held for an additional hour and then cooled. The percentage solids at the end of the reaction was 73.9%. The polymer in solvent appeared slightly hazy with no gel or precipitation present.

Table 1 shows screening experiments using high-fluorine-content acrylic monomers along with TFA (2,2,2-trifluoroethyl acrylate, Synquest Laboratories, Alachua, FL, USA) to disrupt the tendency of high-fluorine-content acrylic monomers to crystallize. Two other fluorinated acrylate monomers, HDFA (1H,1H,2H,2H-heptadecafluorodecyl acrylate, Synquest Laboratories) and HFIPA (hexafluoroisopropyl acrylate, Synquest Laboratories) were also included in the evaluation. AA, as described previously, was used to improve polymer solubility in organic solvent and provide a site for subsequent ionic cross-linking with AAA (aluminum acetylacetonate, Noah Technologies Corp, San Antonio, TX, USA). Pressure-sensitive adhesives typically have a T_g of around 0°C. Therefore, HFBA (experiment 2) and PDFA (experiment 1) appeared to be the most promising candidates because HFBA had the lowest polymer T_g and PDFA had the lowest refractive index with a reasonably low T_g.

TABLE 1 Screening Fluoroacrylic Copolymers

Experiment number	Copolymers ratio 88/10/2	RI		
		%F	Polymer	DSC T_g°C
1	PDFA/TFA/AA	58.9	1.359	11
2	HFBA/TFA/AA	49.7	1.374	0
3	HDFA/TFA/AA	58.5	1.371	51
4	HFIPA/TFA/AA	48.8	1.376	32

TABLE 2 Physical Properties of PDFA/HFBA/AA with Varying Composition

Expt. #	PDFA/ HFBA/ AA weight ratio	%F	Polymer Rl	T_g °C by tan δ max	G' at 20°C dynes/cm^2	Surface energy dyne/cm	% Trans- mittance	Initial peel on glass N/m (lb/in)	50°C peel on glass N/m (lb/in)	50°C peel on HDPE N/m (lb/in)	50°C peel on SS N/m (lb/in)	50°C peel on Teflon N/m (lb/in)
5	93/5/2	60.9	1.356	30	3.3×10^7	9.6	94.2	0.0 cl	18(0.1) jp	0.0 jp	18(0.1) jp	0.0 jp
6	88/10/2	60.4	1.356	25	8.0×10^6	7.6	92.7	70(0.4) jp	53(0.3) jp	18(0.1) jp	88(0.5) jp	18(0.1) jp
7	83/15/2	59.8	1.357	22	2.0×10^6	5.5	94.2	88(0.5) jp	70(0.4) jp	18(0.1) jp	88(0.5) jp	18(0.1) jp
8	78/20/2	59.4	1.357	13	1.5×10^6	3.9	93.9	105(0.6) jp	88(0.5) jp	18(0.1) jp	298(1.7) jp	18(0.1) jp
9	68/30/2	56.3	1.359	13	1.3×10^6	4.2	93.1	123(0.7) jp	298(1.7) jp	18(0.1) jp	280(1.6) jp	18(0.1) jp
10	49/49/2	56.3	1.362	8.5	2.0×10^6	4.1	93.7	228(1.3) jp	385(2.2) cl	35(0.2) jp	333(1.9) cl	18(0.1) jp
11	23/75/2	53.6	1.366	1	1.6×10^6	5.1	94.0	210(1.2) cl	263(1.5) cl	35(0.2) jp	193(1.1) cl	18(0.1) jp
12	49/49/0.2	57.4	1.358	1	4.0×10^5		93.5	228(1.3) jp	280(1.6) cl	53(0.3) jp	245(1.4) cl	70(0.4) jp

"cl" indicates clean peel.

"jp" indicate jerky peel.

Sample 12 cross-linked with 0.05% by weight of AAA.

50°C peel samples were laminated at 50°C and then tested at ambient temperature (23°C).

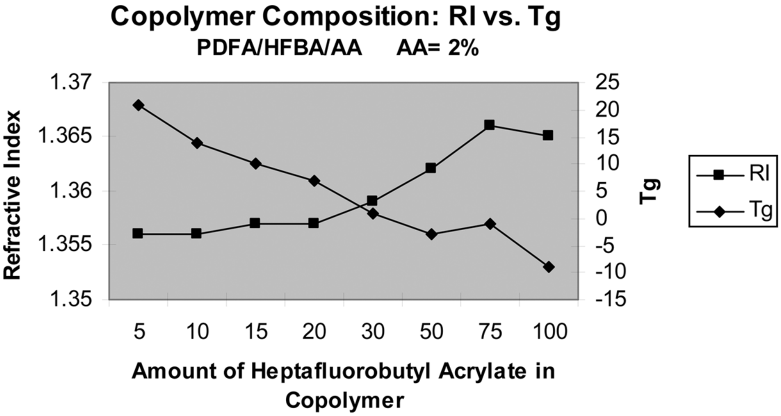


FIGURE 6 PDFA/HFBA/AA copolymer composition effect on refractive index and T_g.

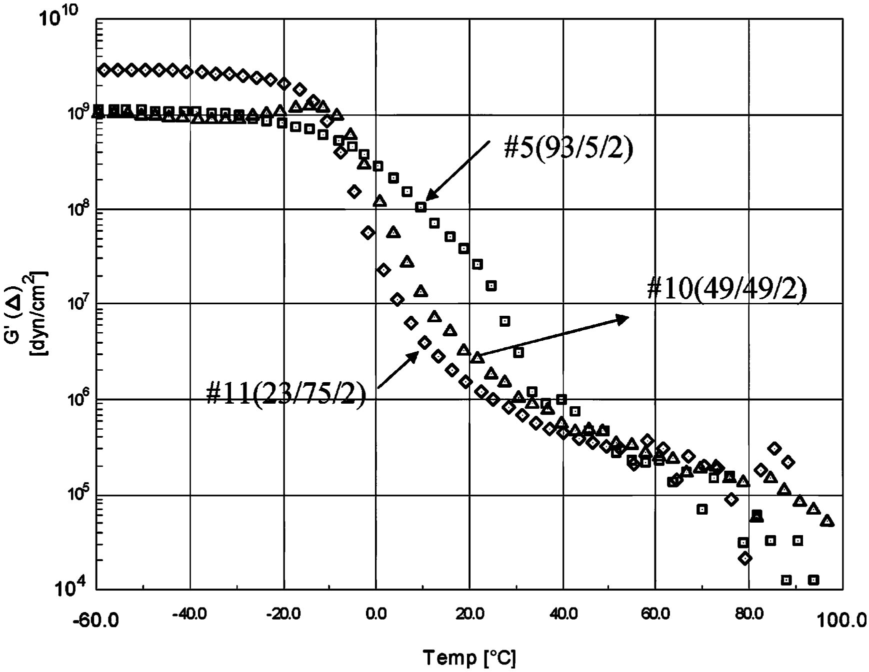


FIGURE 7 Temperature dependence of G' for three different PDFA/HFBA/AA composition polymers.

Correlation of Rheological and Surface Properties With Adhesive Performance

Table 2 shows a series of experiments using PDFA and HFBA at various ratios along with AA. The data show that for the target refractive index (RI < 1.36), the upper limit of HFBA is 30% along with 2% AA (experiment 9). Figure 6 also shows the effects of PDFA/HFBA/AA composition on T_g as well as the refractive index. It is apparent that as the refractive index decreases, the T_g increases correspondingly.

Figures 7 and 8 compare, respectively, the temperature dependence of the dynamic shear storage modulus, G', and viscoelastic index, tan δ, for three PDFA/HFBA/AA polymers with varying ratios of 93/5/2 (*i.e.*, experiment 5), 49/49/2 (*i.e.*, experiment 10), and 23/75/2 (experiment 11). It can be observed that the experiment 5 polymer shows a T_g of 30°C based on the tan δ peak (Figure 8), and the room temperature (20°C) G' is 3.3×10^7 dynes/cm^2, which does not satisfy (*i.e.*, is higher than) the Dahlquist Contact Efficiency Criterion of 3×10^6 dynes/cm^2. However, even though the T_g and room temperature G' of experiment 11

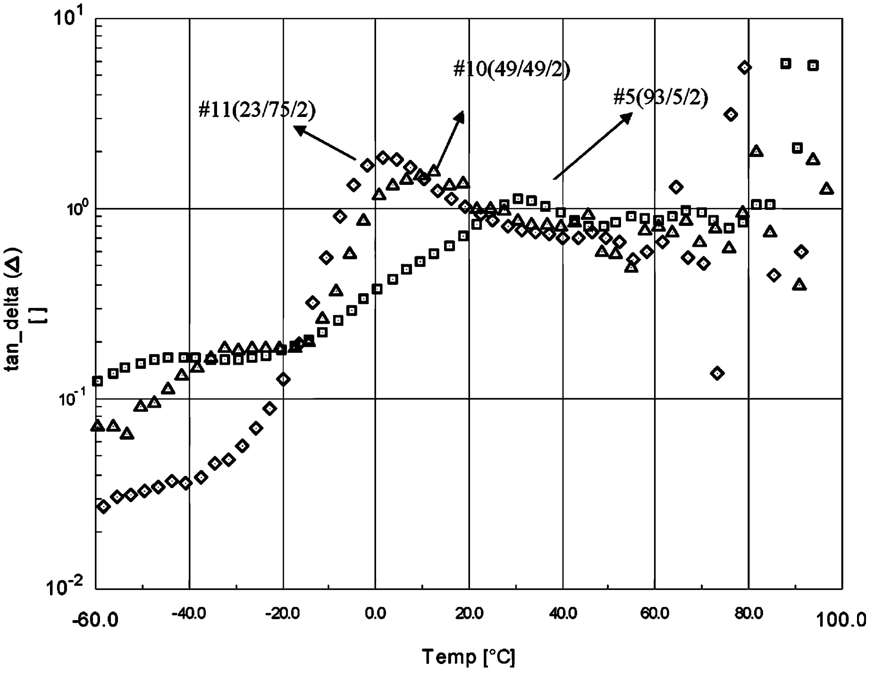


FIGURE 8 Temperature dependence of tan δ for three different PDFA/HFBA/AA composition polymers.

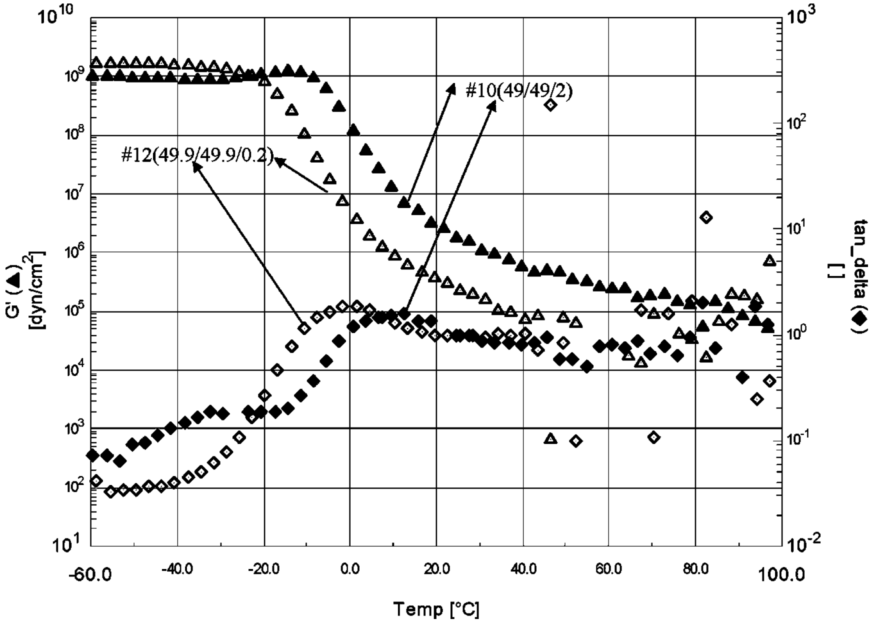
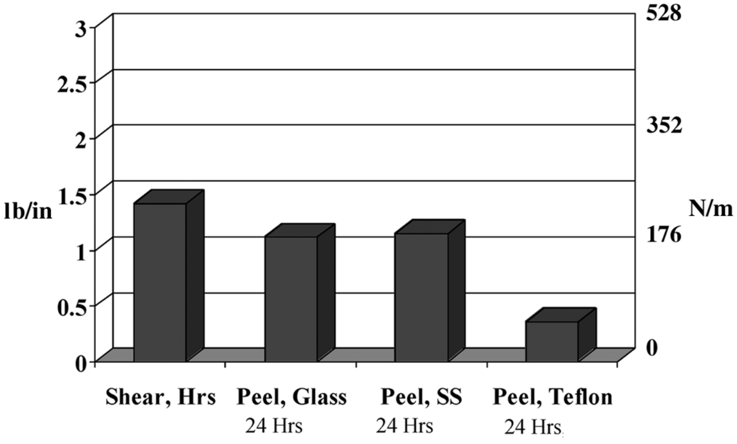


FIGURE 9 Temperature dependence of G' and $\tan\delta$ for 49/49/2 *versus* 49.9/49.9/0.2 PDFA/HFBA/AA polymers.

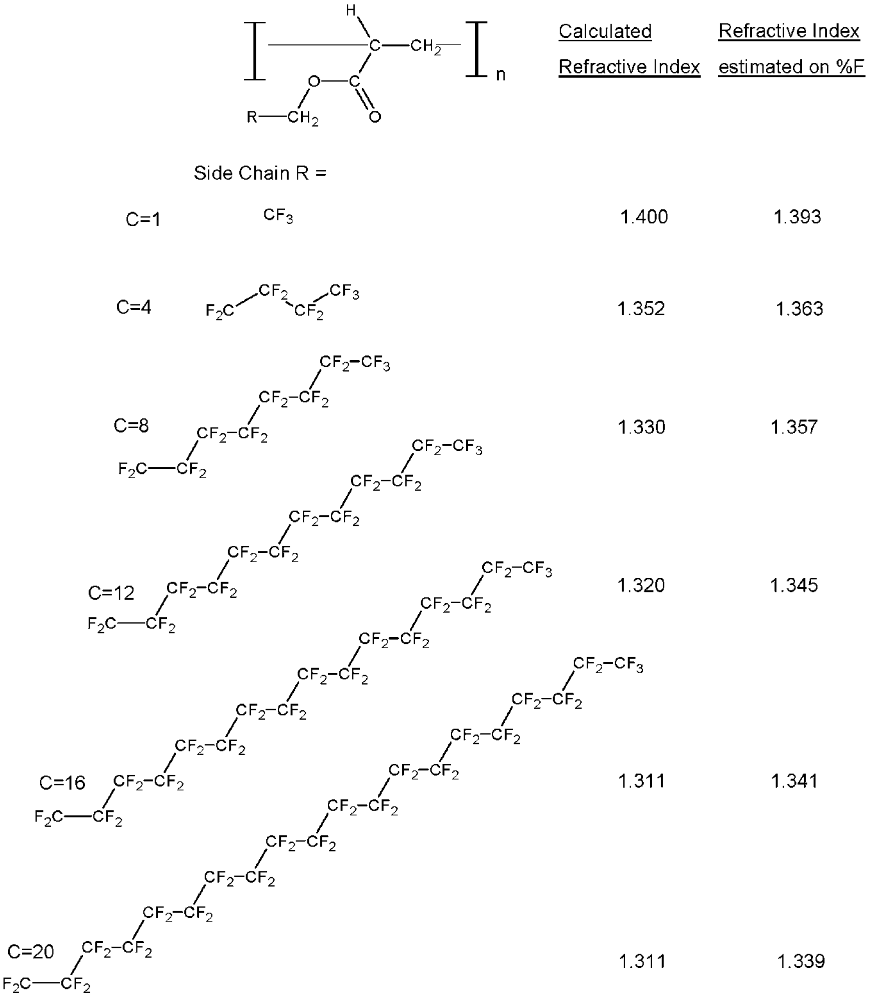


Testing using 2 mil PET film, adhesive at 25-30 g/m²

FIGURE 10 Adhesion performance of a low-refractive-index fluoro-acrylate PSA.

appear be the most favorable for a PSA, its refractive index is slightly too high (1.366). In view of this, experiment 10 polymer was chosen for further improvement of refractive index and adhesion performance.

AA is nonfluorinated and has a higher refractive index than fluorinated acrylics. It is, however, needed for improved polymer solubility and cross-link sites, as well as for specific adhesion to polar surfaces such as glass and stainless steel. To reduce the refractive index further, the concentration of AA was decreased from 2 to 0.2% with



Side Chain R =	Calculated Refractive Index	Refractive Index estimated on %F
C=1	1.400	1.393
C=4	1.352	1.363
C=8	1.330	1.357
C=12	1.320	1.345
C=16	1.311	1.341
C=20	1.311	1.339

FIGURE 11 Theoretical lower limit refractive index of fluoro-acrylate homologs.

TABLE 3 Theoretical Lower Refractive Index Limit of Fluoro-Acrylates Based on Groh and Zimmerman's Model

Polymer repeating unit R=$CH_2-OCO-(CH-CH_2)-$	% Fluorine	R_L molar fraction (cm^3/mol)	V_L molar volume (cc/mol)	M_G, mol. wt of repeating unit (g/mol)	R_L/V_L	Density g/cc (M_G/V_L)	Calc'd. n_D refractive index	Estimated n_D from % fluorine experimental
CF_3	37	24.86	102.2	154	0.244	1.51	1.4	1.393
C_4F_9	56.3	40.03	185.1	304	0.216	1.64	1.352	1.363
C_8F_{17}	60.1	60.29	295.4	504	0.204	1.71	1.33	1.357
$C_{12}F_{25}$	67.5	80.5	405.8	704	0.198	1.735	1.32	1.345
$C_{16}F_{33}$	69.4	100.8	516.8	904	0.193	1.75	1.311	1.341
$C_{20}F_{41}$	70.6	121	627.3	1104	0.193	1.759	1.311	1.339

a 0.1% AAA cross-linker to provide good cohesive strength. The rheological properties of these two copolymers (*i.e.*, experiment 10 and experiment 12) are compared in Figure 9. It is noteworthy that in experiment 12, with lower AA, the refractive index was reduced (1.362 to 1.358), as were both the T_g (6.5 to 1°C based on tan δ peak) and the room temperature G' (3.3×10^6 to 4×10^5 dynes/cm^2).

From the bulk properties viewpoint, the lower T_g and lower room temperature G' would predict a better PSA. This is reflected in the increase in peel adhesion against low surface-energy substrates high density poly(ethylene) (HDPE) (0.2 to 0.3 lb/in, 35 to 53 N/m) and Teflon® (0.1 to 0.4 lb/in, 18 to 70 N/m) [9]. However, lower peel adhesion against high-surface-energy substrates such as glass (2.2 to 1.6 lb/in, 387 to 281 N/m) and SS (1.9 to 1.4 lb/in, 334 to 246 N/m) was also observed (Fig. 10). This reversed trend is consistent with the 10-fold decrease in AA, an adhesion promoter. A larger lab-batch polymer was subsequently made. The polymer content and viscosity in a nonhalogenated solvent were, respectively, 69% and 3290 cPs. It is noteworthy that, at this viscosity, these fluoro-acrylate polymers can be made in nonhalogenated solvents with a viscosity range compatible with industrial coaters.

Refractive-Index Limits of Fluoro-acrylate Polymers

Figure 11 and Table 3 show the predicted refractive index of a homologous series of fluoro-acrylates with increased number of repeating CF_2 units in the side chain based on Groh and Zimmerman's model. As the number of CF_2 units increases, the refractive index decreases progressively and approaches a lower limit of 1.29 with the number of CF_2 units approaching infinity. For the fluoro-acrylate polymer to be a PSA, it needs to be copolymerized with other monomers such as other side-chain fluoro-acrylates and AA, which increases the refractive index. It is believed that a value of 1.36 in this work is approaching the lower limit for a functional PSA against both high- and low-surface-energy substrates. This work demonstrated that a good balance of low refractive index with good pressure-sensitive adhesion was achieved through the interplay of both polymer chemistry and physics.

CONCLUSIONS

- A good balance of low refractive index (<1.36), optical clarity, and good pressure-sensitive adhesion has been achieved through the interplay of polymer chemistry (employing side-chain fluoro-acrylates) and physics (material properties of T_g, rheology, and surface energy).

- These fluoro-acrylated polymers can be made in nonhalogenated solvents with a viscosity range enabling them to be coated with industrial coaters.
- Crystallization of polymer (main or side chain) increases the predicted refractive index as well as decreases the contact efficiency of PSAs.
- Lower refractive index with higher fluorine content raises the T_g.
- The theoretical lower-refractive-index limit of fluorinated acrylic polymers is predicted to be around 1.29. It is believed that a refractive index value of 1.36 is approaching the lower limit for a functional PSA.

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