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(54) 【発明の名称】高い屈折率および低いガラス転移温度を有するナフチロキシアルキル（メタ）アクリレート

(57)【要約】
高い屈折率を有し、そのそれぞれのホモポリマーが低いガラス転移温度を有する、ナフチロキシアルキル（メタ）アクリレートモノマー。

【特許請求の範囲】

【請求項１】

約１．５５を越える屈折率を有し、そのそれぞれのホモポリマーが約１０℃未満のガラス転移温度を有する、ナフチロキシアルキル（メタ）アクリレートモノマー。

【請求項２】

少なくとも６個の炭素原子を有するアルキル官能基を含む、ナフチロキシアルキル（メタ）アクリレートモノマー。

【請求項３】

前記モノマーが約１．５５を越える屈折率を有し、そのそれぞれのホモポリマーが約１０℃未満のガラス転移温度を有する、請求項２に記載のモノマー。

【請求項４】

前記アルキル基が６個の炭素原子を有する、請求項２に記載のモノマー。

【請求項５】

前記アルキル基が８個の炭素原子を有する、請求項２に記載のモノマー。

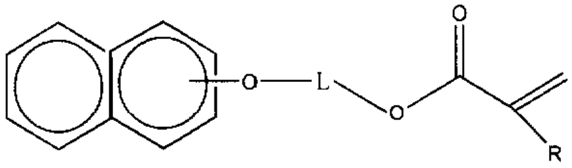
【請求項６】

前記アルキル基が直鎖である、請求項２に記載のモノマー。

【請求項７】

次式２のモノマー：

【化１】



式2

（式中、Ｌは炭素原子が５個を越える直鎖または分枝鎖アルキル基であり、ＲはＨまたはＣH_3である。）。

【請求項８】

式中のＬが炭素原子６～８個の直鎖アルキル単位である、請求項７に記載のモノマー。

【請求項９】

式中のＬが炭素原子６個の直鎖アルキル単位である、請求項７に記載のモノマー。

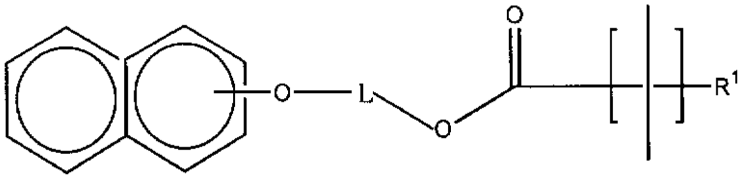
【請求項１０】

請求項７に記載のモノマーを含む、重合性組成物。

【請求項１１】

次式３の化学セグメントを含むポリマー：

【化２】



式３

（式中、Ｌは約５個を越える炭素原子を有する直鎖または分枝鎖アルキル基であり、R^1はＨまたはCH_3である。）。

【請求項１２】

請求項１１に記載のポリマーを含む光学素子。

【請求項１３】

請求項１１に記載のポリマーを含む光学素子を含む、光学装置。

【請求項１４】

請求項１１に記載のポリマーを基材に塗布するステップを含む、基材上のグレアを低下させる方法。

【発明の詳細な説明】

【０００１】

技術分野

本発明は、高い屈折率を有し、そのそれぞれのホモポリマーが低いガラス転移温度を有する、ナフチロキシアルキル（メタ）アクリレート化合物に関する。

【０００２】

背景

光学用途で使用される接着剤またはコーティングは、好ましくはそれらが塗布される基材の屈折率に密接に適合した屈折率を有する。適合した屈折率は、基材とコーティング材料間の界面におけるグレアおよび反射率を低下させ、構造物の光学性能を向上させる。

【０００３】

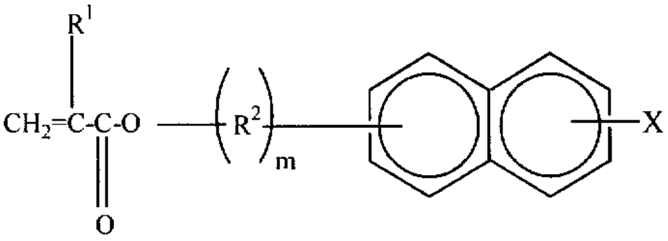
典型的に光学用途で使用される高分子基材材料は、例えばポリメチル（メタ）アクリレート（１．４８９）、ポリカーボネート（１．５８５）、およびポリエチレンテレフタレート（１．６４）などのように約１．４８～約１．６５の屈折率を有する。しかしこれらの基材に塗布することを意図する高分子コーティングおよび接着剤の多くは、基材の屈折率と実質的に異なる屈折率を有する。この適合していない屈折率は、材料間の界面でグレアおよび反射率を引き起こすかもしれない。

【０００４】

反応性化学モノマーは、単独でまたは他の材料と組み合わせて使用して、高い屈折率を有する接着剤およびコーティングが製造できる。しかしこれらの接着剤およびコーティング組成物は、他のより望ましくない物理的および化学的特性を有するかもしれない。例えば下の式１の特定のナフタレン誘導体：

【０００５】

【化３】



式１

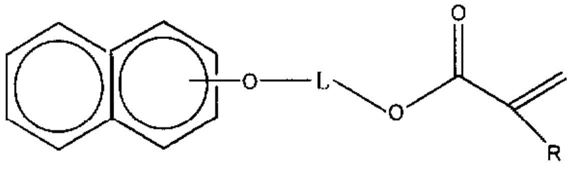
【０００６】
（式中、Ｒ^{1}はＨまたはＣＨ$_3$であり、Ｒ^{2}はＣＨ$_2$ＣＨ$_2$ＯまたはＣＨ（ＣＨ$_3$）ＣＨ$_2$Ｏであり、ＸはＨであり、ｍは１である。）は、約１．５７～１．５８の屈折率を有する。式１のモノマーの屈折率は、光学用途で一般に使用される高分子基材に良く適合するかもしれないが、このタイプの既知の化合物から製造されるホモポリマーは、典型的に約２５～約４０℃のガラス転移温度（Ｔｇ）を有する。そのため、これらのモノマー単位を含むポリマーは、室温（約２０～約３０℃）前後で実質的に非粘着性であることが予期され、光学接着剤および可撓性コーティングにおけるそれらの有用性が制限される。

【０００７】
概要

一つの面では、本発明は、約１．５５を越える屈折率を有し、そのそれぞれのホモポリマーのガラス転移温度が約１０℃未満である、ナフチロキシアルキル（メタ）アクリレートモノマーにある。ナフチロキシアルキル（メタ）アクリレートモノマーは、アルキル官能基によって結合された、（メタ）アクリレート官能基とナフチロキシ官能基とを含む。

【０００８】
本発明の好ましいナフチロキシアルキル（メタ）アクリレートモノマーは、一般式２：

【０００９】
【化４】



式２

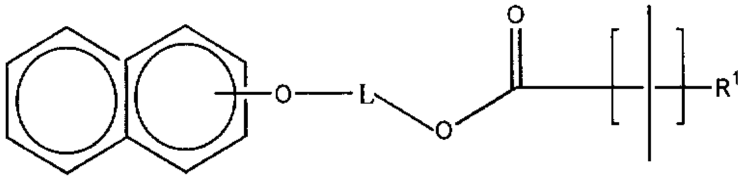
【００１０】
（式中、Ｌは５個を越える炭素原子、好ましくは約６～約８個の炭素原子を有する直鎖または分枝鎖アルキル基であり、ＲはＨまたはＣＨ$_3$である。）を有する。

【００１１】
第２の面では、本発明は、式２のモノマーを含有する重合性組成物にある。この重合性組成物は、１つ以上の他の適合性のコモノマーを含有することができる。

【００１２】
第３の面では、本発明は、式３：

【００１３】

【化５】



式３

【００１４】
（式中、Ｌは５個を越える炭素原子、好ましくは約６～約８個の炭素原子を有する直鎖または分枝鎖アルキル基であり、Ｒ^{1}はＨまたはＣＨ$_{3}$である。）の化学セグメントを含むポリマーまたは高分子材料にある。式３のモノマーセグメントを有するポリマーは、約１０℃未満の低いガラス転移温度を有し、光学接着剤および可撓性コーティング組成物中で使用するのに良く適している。本発明のモノマーから製造される接着剤およびコーティング組成物は、同様に高い屈折率を有する高分子基材に塗布した際に、グレアおよび反射率を低下させることが予期される。

【００１５】
第４の面では、本発明は、式３のセグメントを有するポリマーまたは高分子材料を有する組成物を含む、光学素子にある。

【００１６】
第５の面では、本発明は、式３のセグメントを有するポリマーまたは高分子材料を有する組成物を含む、光学装置にある。

【００１７】
第６の面では、本発明は、式３のセグメントを有するポリマーまたは高分子材料を有する組成物で基材をコーティングするステップを含む、基材上のグレアおよび／または反射率を低下させる方法にある。

【００１８】
本発明の１つ以上の実施態様の詳細を下記の説明に記載する。本発明のその他の特色、目的、および利点は、説明および特許請求の範囲から明らかになるであろう。

【００１９】
詳細な説明

本発明は、高い屈折率を有し、そのそれぞれのホモポリマーが低いガラス転移温度を有する、ナフチロキシアルキル（メタ）アクリレートモノマーである。モノマーは、光学素子または光学装置の基材に塗布することを意図する高分子材料中で使用するのに特に適した、特定の屈折率、融点、および粘度特性を有する。

【００２０】
本明細書中で使用した場合、「モノマー」とは、個々の（すなわち分子）スケールのモノマーを指し、また組成物が、物質の物理的状態（例えば液体、固体など）および物理的特性（例えば融点、粘度、（高分子形態の）ガラス転移温度、および屈折率）を有すると言えるような、このようなモノマーの巨視的スケールの組成物も指す。

【００２１】
本発明のナフチロキシアルキル（メタ）アクリレートモノマーは、少なくとも約１．５４、好ましくは約１．５４～１．５６の屈折率を有する。「屈折率（ｉｎｄｅｘ　ｏｆ　ｒｅｆｒａｃｔｉｏｎ）」または「屈折率（ｒｅｆｒａｃｔｉｖｅ　ｉｎｄｅｘ）」とは、放射線が波長約５８３．９ｎｍのナトリウムイエローライトである場合の自由空間内の電磁放射線速度と、材料内の放射線速度との比率であると理解される、材料（例えばモノマ

ー）の絶対屈折率を指す。屈折率は既知の方法によって測定でき、概してアッベ屈折計を使用して測定される。

【００２２】

本発明のナフチロキシアルキル（メタ）アクリレートモノマーのホモポリマーは、約１０℃未満、好ましくは約７℃未満、そして最も好ましくは約５℃未満のＴｇを有する。「ガラス転移温度」（Ｔｇ）とは、熱可塑性ポリマーがもろいガラス状態から可塑性状態に変化する温度範囲である。組成物のガラス転移温度は、示差走査熱分析（ＤＳＣ）、被変調ＤＳＣ（ＭＤＳＣ）、または動的機械分析（ＤＭＡ）などの技術分野で既知の方法によって測定できる。

【００２３】

ナフチロキシアルキル（メタ）アクリレートモノマーは、アルキル官能基によって結合された、（メタ）アクリレート官能基とナフチロキシ官能基とを含む。

【００２４】

アルキル基は、二価の有機炭化水素基である。好ましくは非置換であるアルキル基は直鎖または分枝鎖であることができ、５個を越える炭素原子、より好ましくは６～８個の炭素原子を含む。アルキル基のサイズは、例えばモノマーの屈折率、およびモノマーから調製されるポリマーの屈折率およびガラス転移温度をはじめとする、モノマーおよびモノマーから調製されるポリマーの物理的特性に影響できる。いかなる理論による拘束も望まないが、比較的より小さいアルキル基を有するその他の点では同様のモノマーまたはポリマーと比べて、比較的より大きいアルキル基からは、比較的より低い屈折率を有するモノマーまたはポリマーが得られるかもしれない。ふたたびいかなる理論による拘束も望まないが、比較的より小さいまたは分枝がより少ない分枝鎖アルキル基を有するその他の点では同様のモノマーから調製されるポリマーと比べて、比較的より大きいまたは分枝がより多い分枝鎖アルキル基は、重合した際に比較的より低いＴｇを有するモノマーを提供するかもしれない。

【００２５】

本発明のモノマー中のナフチロキシ基もまた、好ましくは非置換である。

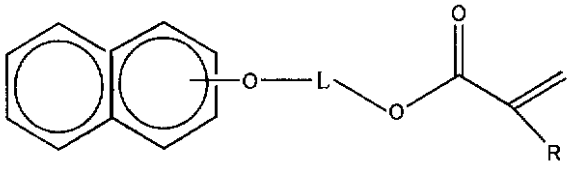
【００２６】

本発明のモノマー中の（メタ）アクリレート基は、当業者に周知の方法によって調製できる。ナフチロキシアルカノール中間体は、適切な塩基を使用して塩化（メタ）アシロイルと共にエステル化できる。それらは（メタ）アクリル酸との縮合によって、または例えばメチル（メタ）アシレートを使用したエステル転移反応によっても調製できる。モノマー合成中に適切な抑制剤を反応に添加して、モノマーの早期重合を防止できる。

【００２７】

有用なナフチロキシアルキルアクリレートモノマーの例としては、式２の構造：

【化６】



式２

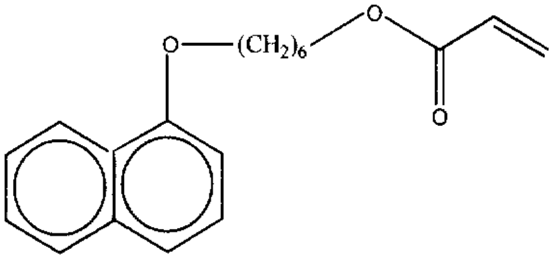
（式中、Ｌは５個を越える炭素原子、好ましくは約６～約８個の炭素原子を有する直鎖または分枝鎖アルキル基であり、ＲはＨまたはCH_3である。）を有するものが挙げられる。

【００２８】

有用なモノマーの例としては、オキシアルキルアクリレート基がナフタレン環構造の１またはα位にあり、アルキル単位が６個の炭素原子を有する、６－（１－ナフチロキシ）－１－ヘキシルアクリレートが挙げられる。下の式４に示すこのモノマーは、約１．５５６の屈折率を有し、そのホモポリマーのＴｇは約３℃である。

【００２９】

【化７】



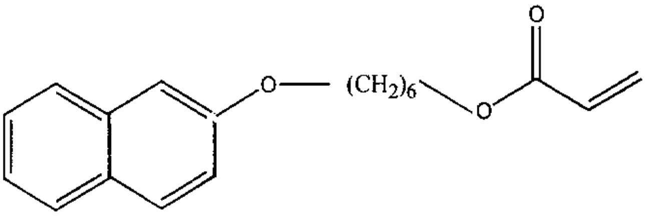
式４

【００３０】

他の好ましいモノマーは、オキシアルキルアクリレート基がナフタレン環構造の２またはβ位にあり、アルキル単位が６個の炭素原子を有する、６－（２－ナフチロキシ）－１－ヘキシルアクリレートである。下の式５に示すこのモノマーは、約１．５５３の屈折率を有し、ホモポリマーのＴｇは約６℃である。

【００３１】

【化８】



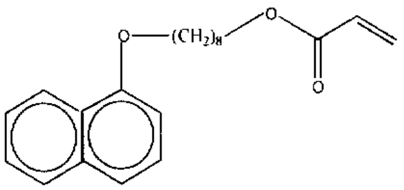
式５

【００３２】

他の好ましいモノマーは、オキシアルキルアクリレート基がナフタレン環構造の１またはα位にあり、アルキル単位が８個の炭素原子を有する、８－（１－ナフチロキシ）－１－オクチルアクリレートである。下の式６に示すこのモノマーは、約１．５４７の屈折率を有し、そのホモポリマーのＴｇは約－４９℃である。

【００３３】

【化９】

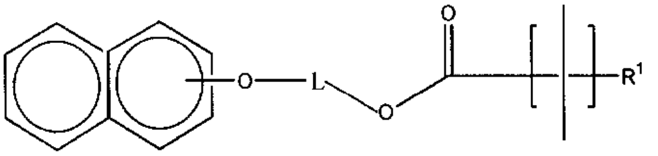


式６

【００３４】
本発明のモノマーは、単独でまたは他の不飽和の重合性コモノマーなどの材料と組み合わせて、重合または共重合されて有用なポリマーまたは共重合体を生じることができる、重合性組成物内に含まれることができる。本明細書において使用した場合、「重合性」という用語は、（例えば不飽和部分を通じて）重合または共重合されて、オリゴマー、ポリマー、プレポリマーまたは高分子材料などのより高分子量の材料を生じることができる、モノマーおよびオリゴマーなどの化合物と、化学組成物とを指す。「ポリマー」および「高分子材料」と言う用語は互換的に使用され、二量体、三量体、オリゴマー、共重合体、ホモポリマーなどを生じる、例えば１つ以上の重合性モノマー、オリゴマー、ポリマー、またはプレポリマーなどの１つ以上の重合性材料の反応から調製される材料を指す。

【００３５】
ポリマーおよび高分子材料は、式３の化学セグメント：

【００３６】
【化１０】



式３

【００３７】
（式中、Ｌは好ましくは５個を越える炭素原子、好ましくは約６～約８個の炭素原子を有する直鎖または分枝鎖アルキル基であり、R^1はＨまたはCH_3である。）を含む。

【００３８】
ここで述べるモノマーのような、アクリルモノマーと反応する有用なコモノマーは有機化学の技術分野で既知であり、例えばビニル、（メタ）アクリレート、Ｎ－ビニル、アクリル酸、メタクリル酸、アリル、アクリルアミド、アクリロニトリルなどのいくつかの既知で有用な重合性部分のいずれをも含むことができる。コモノマーは、不飽和部分に関して単官能性または多官能性であることができ、多官能性の場合、不飽和部分は必ずしも同一の化学的性質でなくても良い。

【００３９】
重合性組成物中で有用な特定タイプのコモノマーとしては、ブチル（メタ）アクリレートなどの（メタ）アクリレート官能基コモノマー、ならびにメチルスチレンなどのビニルコモノマーを挙げることができる。あらゆる任意の重合性組成物に含まれる特定のコモノマー、それらの分子量（単数または複数）、およびそれぞれの含有量は、重合性組成物の所望の性質および特性、およびそれから調製されるポリマーまたは高分子材料の所望の特性

など（例えば重合性組成物または高分子材料の屈折率、ガラス転移温度、融点、粘度など）の様々な要素次第で選択できる。

【００４０】

重合性組成物は、高分子材料の当業者によって理解されるように、このような重合性組成物中で有用であることができる他の成分を含有することができる。例えば重合性組成物は、架橋剤、１つ以上の界面活性剤、顔料、充填剤、重合抑制剤、あるいは重合性組成物または光学製品中で有用であることができるその他の成分を含有してもよい。このような成分は、それらのそれぞれの目的に効果的な既知の量で組成物中に含めることができる。

【００４１】

架橋剤は、重合性組成物の架橋に起因する、ポリマーのガラス転移温度の増大に有用であることができる。

【００４２】

処理を改善するため、重合された材料に滑りおよびスクラッチ抵抗性を与えるため、あるいは重合された材料の光学特性に影響を及ぼすために、重合性組成物に高分子ビーズ、無機充填剤、および／または顔料を添加できる。有用な高分子ビーズの例としては、ポリスチレン、ポリアクリレート、スチレンとアクリレートとの共重合体、ポリエチレン、ポリプロピレン、ポリテトラフルオロエチレン、またはそれらの組み合わせからできたものが挙げられる。無機充填剤および顔料の例としては、中実または中空ガラスビーズ、シリカ、ジルコニア、三水酸化アルミニウム、および二酸化チタンが挙げられる。

【００４３】

重合性組成物の重合は、ラジカル重合剤の存在下での加熱、適切な光重合開始剤の存在下での紫外線または可視光などの電磁放射線の照射、および電子ビームなどの既知かつ通常の手段によって達成できる。

【００４４】

本発明のモノマーから調製される高分子材料（すなわちホモポリマーまたは共重合体）は、約１０℃未満のＴｇならびに約１．５４を越える屈折率を有する。これによってポリマーは、光学素子および光学装置内で使用される、例えばポリメチルメタクリレート（ＰＭＭＡ）、ポリカーボネート（ＰＣ）、およびポリエチレンテレフタレート（ＰＥＴ）などの高分子基材上で、コーティングおよび接着剤として使用するのに特に良く適するようになる。例えば同時係属の米国特許出願第０９／６０５，５００号で述べられるように、本発明のモノマーから調製されるポリマーを使用して光学装置中の基材に塗布するための感圧接着剤を製造しても良い。また本発明のモノマーから調製されるポリマーを光学装置中の光学素子のためのコーティングとして使用しても良い。

【００４５】

従来のポリマーと比べて、本発明のモノマーから製造されるポリマーは、光学素子および装置内で一般に使用される、高分子基材の屈折率により密接に適合した屈折率を有する。この屈折率の適合は、基材とポリマー間のあらゆる光学界面におけるグレアおよび反射率を低下させるので、本発明のモノマーから製造されるポリマーを基材上のグレアおよび／または反射率を低下させるための方法の一部として使用しても良い。この方法は、式３のフラグメントを有するポリマーまたは高分子材料を有する組成物で基材をコーティングするステップを含む。

【００４６】

「グレア」という用語は、ここで使用した場合、約４００〜約７００ｎｍの範囲にわたる平均反射率を意味する。「反射率」という用語は、その底面が表面であって入射放射線を包含する同一半球内に戻る、表面上の入射放射束の分率を意味する。

【００４７】

本発明は、以下の制限を意図しない実施例を参照すればより完全に理解されるであろう。なお、実施例において、反応成分は使用グラム数（ｇ）で、あるいは公称１００重量％の反応混合物総重量を基準とした重量％で表わされる。英国法単位の寸法が公称であり、メートル法単位への換算は近似値である。

【００４８】
実施例１
６－（１－ナフチロキシ）－１－ヘキシルアクリレート（１－ＮＯＨＡ）の合成
１Ｌ容三つ口フラスコに、撹拌機、温度プローブ、および冷却管を装着した。以下の試薬を添加した：５０ｇの１－ナフトール、３１２ｇの脱イオン水、５．２ｇのヨウ化ナトリウム、および５５．４ｇの水酸化ナトリウム（水中５０％）。混合物を加熱して還流させた。還流反応物に、２時間にわたり添加漏斗を通じて９４．７ｇの６－クロロ－１－ヘキサノールを滴下して添加した。添加完了後、還流点での加熱をさらに１時間継続した。ガスクロマトグラフィー（ＧＣ）分析からは、１％未満の残留開始材料が示された。

【００４９】
反応物を室温に冷却した。３６６ｇのｔ－ブチルメチルエーテルを添加した。反応混合物を撹拌し、次に分液漏斗に注いで相分離させた。水相を除去し、有機相を１２５ｇの脱イオン水中の６．９ｇの濃ＨＣｌ、次に１２５ｇの脱イオン水中の６．１ｇのＮａＣｌで洗浄した。回転蒸発機を使用して、生成物から残留溶剤を除去した。

【００５０】
０．１～０．２ｍｍＨｇにおいてポット温度２２０～２６０℃およびヘッド温度２００～２３０℃で、生成物を蒸留した。この手順によって、６３．５ｇの淡褐色でいくらか粘稠な液体が得られた。ＧＣからは、それが少なくとも９８％純粋な６－（１－ナフチロキシ）－１－ヘキサノールであることが示された。

【００５１】
撹拌機、温度プローブ、および冷却管付きＤｅａｎ－Ｓｔａｒｋトラップを装着した１Ｌ容三つ口フラスコに、以下の試薬を添加した：６０ｇの６－（１－ナフチロキシ）－１－ヘキサノール、２２６ｇのトルエン、２．５ｇのパラートルエンスルホン酸、２１．２ｇのアクリル酸、０．０２７ｇのヒドロキノン、および０．０３ｇの４－メトキシフェノール。混合物を加熱して環流させ、Ｄｅａｎ－Ｓｔａｒｋトラップ内に放出された水を捕集した。３時間後、反応が完了した（すなわち開始材料の残留がない）ことが薄層クロマトグラフィーから示された。

【００５２】
反応物を室温に冷却し、１３２ｇの脱イオン水を添加した。混合物を分液漏斗入れて振盪して相分離させた。水相を除去して、有機相を４４ｇの脱イオン水中の０．３ｇの濃ＨＣｌ、次に４４ｇの脱イオン水中の１．３ｇの炭酸ナトリウム、そして次に４４ｇ脱イオン水中の１．４ｇの塩化ナトリウムで洗浄した。回転蒸発機を使用して、残留溶剤を除去した。粗生成残留物をフラッシュシリカゲルカラムに通過させて、酢酸エチル／ヘプタン（５／９５）の混合物で溶出した。生成物分画を捕集して、回転蒸発機を使用して溶剤を除去した。淡い緑がかった油生成物を静置すると、結晶化して融点３７～３９℃のオフホワイトの結晶４５ｇが得られた。ＧＣおよび^{13}Ｃ　ＮＭＲ分析によって、生成物が９９％を越える純度の６－（１－ナフチロキシ）－１－ヘキシルアクリレート（１－ＮＯＨＡ）であることが確認された。

【００５３】
日本国東京在のＥｒｍａ　Ｉｎｃ．が製造しＦｉｓｈｅｒ　Ｓｃｉｅｎｔｉｆｉｃによって流通されるアッベ屈折計を使用して測定された１－ＮＯＨＡの屈折率は、１．５５６であった。

【００５４】
１２０ｍｌ容ボトルに２．０ｇの１－ＮＯＨＡモノマー、１０ｇの酢酸エチル、およびデラウェア州ウィルミントンのＥ．Ｉ．ＤｕＰｏｎｔ　Ｄｅ　Ｎｅｍｏｕｒｓ　ａｎｄ　Ｃｏ．からＶＡＺＯ　６４の商品名の下に入手される０．０６ｇの触媒を装填して、ホモポリマーを調製した。分速１Ｌの流速で３５秒間窒素パージして、ボトルを脱酸素化した。次にボトルを密封し、５５℃の回転水浴内に２４時間入れて実質的に完全な重合を達成した。ポリマー溶液をアルミニウムパン内にキャストして、溶剤を６５℃のオーブン内で蒸発させてポリマーフィルムを調製した。コネチカット州のノーウォークのＰｅｒｋｉｎ

Elmerによって製造された示差走査熱量計（DCS－7）を使用して、ガラス転移温度（Tg）を測定した。10mgのポリマーサンプルを20℃／分の速度で加熱して、40℃／分の速度で冷却し、次に20℃／分で再度加熱した。2回目の加熱サイクルでTgを計算したところ6℃であった。

【0055】

実施例2

8－（1－ナフチロキシ）－1－オクチルアクリレート（1－NOOA）の合成

500ml容三つ口フラスコに、撹拌機、温度プローブ、および冷却管を装着した。以下の試薬を添加した：25gの1－ナフトール、156gの脱イオン水、2．6gのヨウ化ナトリウム、および27．7gの水酸化ナトリウム（水中50％）。この混合物を加熱して還流させた。還流反応物に、2時間にわたり添加漏斗を通じて57．1gの8－クロロ－1－オクタノールを滴下して添加した。添加完了後、還流点での加熱をさらに1時間継続した。ガスクロマトグラフィー（GC）分析からは、1％未満の残留開始材料が示された。

【0056】

反応物を室温に冷却し、207gのクロロホルムを添加した。混合物を撹拌し、次に分液漏斗に注いで相分離させせた。上方の水相を分離して、有機相を62gの脱イオン水中の3．4gの濃HCl、次に62gの脱イオン水中の3．0gのNaClで洗浄した。回転蒸発機を使用して、生成物から溶剤を除去した。

【0057】

次に生成物を蒸留し、最初に0．2mmHgで約100℃のヘッド温度で残留8－クロロ－1－オクタノールを除去した。生成物は0．1mmHgで180～200℃のヘッド温度で蒸留された。淡いオレンジ色の8－（1－ナフチロキシ）－1－オクタノールが約17g捕集された。

【0058】

250ml容三つ口フラスコに、撹拌機、温度プローブ、および冷却管付きDean－Starkトラップを装着した。以下の試薬を添加した：14gの8－（1－ナフチロキシ）－1－オクタノール、118gのトルエン、0．5gのパラートルエンスルホン酸、4．5gのアクリル酸、0．006gのヒドロキノン、および0．006gの4－メトキシフェノール。混合物を加熱して環流させ、Dean－Starkトラップ内に放出された水を捕集した。3時間後、反応が完了したことが薄層クロマトグラフィーから示された。

【0059】

反応物を室温に冷却し、27gの脱イオン水を添加した。混合物を分液漏斗内で良く振盪して相分離させ、水相を除去した。有機相を10gの脱イオン水中の0．1gの濃HCl、次に10gの脱イオン水中の0．3gの炭酸ナトリウム、次に10gの脱イオン水中の0．3gの塩化ナトリウムで順次洗浄した。回転蒸発機を使用して溶剤を除去した、粗生成残留物をフラッシュシリカゲルカラムに通過させて、塩化メチレンで溶出した。生成物分画を捕集して、回転蒸発機を使用して溶剤を除去し、最後に真空ポンプでフラスコを吸引して最後の痕跡量の溶剤を除去した。

【0060】

淡黄色油生成物は静置すると結晶化して、12gの湿った半固体が得られた。GCおよび^{13}C NMRから、生成物が99％を越える純度の8－（1－ナフチロキシ）－1－オクチルアクリレート（1－NOOA）であることが確認された。

【0061】

日本国東京在のErma Inc.が製造しFisher Scientificによって流通されるアッベ屈折計を使用して測定された1－NOOAの屈折率は、1．547であった。

【0062】

1－NOHAの代わりに1－NOOAを使用したこと以外は、実施例1で述べたようにしてホモポリマーを調製した。ホモポリマーのTgは－49℃であった。

【００６３】
本発明の実施態様の多数について述べた。それでもやはり、本発明の精神と範囲を逸脱することなく、様々な変更ができるものと理解される。従って他の実施態様は、特許請求の範囲内にある。

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(54) **Title:** NAPHTHYLOXYALKYL (METH) ACRYLATES WITH HIGH REFRACTIVE INDICES AND LOW GLASS TRANSITION TEMPERATURES

(57) **Abstract:** Naphthyloxyalkyl(meth)acrylate monomers having a high refractive index and whose respective homopolymer has a low glass transition temperature.

NAPHTHYLOXYALKYL(METH)ACRYLATES WITH HIGH REFRACTIVE INDICES AND LOW GLASS TRANSITION TEMPERATURES

TECHNICAL FIELD

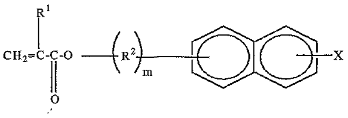
This invention relates to naphthyloxyalkyl(meth)acrylate compounds with a high refractive index and whose respective homopolymer has a low glass transition temperature.

BACKGROUND

Adhesives or coatings used in optical applications preferably have a refractive index closely matched to the refractive index of a substrate to which they are applied. The matched refractive indices reduce glare and reflectance at the interface between the substrate and coating materials and enhance the optical performance of the construction.

Polymeric substrate materials typically used in optical applications have refractive indices of about 1.48 to about 1.65, such as, for example, polymethyl(meth)acrylate (1.489), polycarbonate (1.585), and polyethylene terephthalate (1.64). However, many polymeric coatings and adhesives intended for application to these substrates have refractive indices that differ substantially from the refractive indices of the substrates. The mismatched refractive indices may cause glare and reflectance at the interface between the materials.

Reactive chemical monomers can be used, alone or in combination with other materials, to produce adhesives and coatings with high indices of refraction. However, these adhesive and coating compositions may have other less desirable physical and chemical properties. For example, certain naphthalene derivatives of Formula 1 below have an index of refraction of about 1.57 - 1.58:



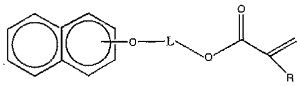
Formula 1

wherein R^1 is H or CH_3, R^2 is CH_2CH_2O or $CH(CH_3)CH_2O$, X is H, and m is 1. While the refractive index of the monomers in Formula 1 may match well with polymeric substrates commonly used in optical applications, homopolymers made from known compounds of this type typically have a glass transition temperature (Tg) of about 25 to about 40 °C. For this reason, polymers including these monomeric units would be expected to be essentially non-tacky at or near room temperature (about 20 to about 30 °C), which limits their usefulness in optical adhesives and flexible coatings.

SUMMARY

In one aspect, the invention is a naphthyloxyalkyl(meth)acrylate monomer with an index of refraction of greater than about 1.55 and a glass transition temperature of its respective homopolymer of less than about 10 °C. The naphthyloxyalkyl(meth)acrylate monomers include a (meth)acrylate functional group and a naphthyloxy functional group linked by an alkyl functional group.

The preferred naphthyloxyalkyl(meth)acrylate monomers of the invention have the general Formula 2:

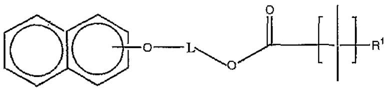


Formula 2

wherein L is a straight chain or branched alkyl group containing greater than 5 carbon atoms, preferably from about 6 to about 8 carbon atoms, and R is H or CH_3.

In a second aspect, the invention is a polymerizable composition containing the monomer of Formula 2. The polymerizable composition can contain one or more other compatible comonomers.

In a third aspect, the invention is a polymer or polymeric material including a chemical segment of Formula 3:



Formula 3

wherein L is a straight chain or branched alkyl group containing greater than 5 carbon atoms, preferably from about 6 to about 8 carbon atoms, and R^1 is H or CH_3. The polymers with the monomeric segment of Formula 3 have a low glass transition temperature of less than about 10 °C, and are well suited for use in optical adhesives and flexible coating compositions. The adhesives and coating compositions made from the monomers of the invention would be expected to reduce glare and reflectance when applied to a polymeric substrate with a similarly high refractive index.

In a fourth aspect, the invention is an optical element including a composition with the polymer or polymeric material with the segment of Formula 3.

In a fifth aspect, the invention is an optical device including a composition with the polymer or polymeric material with the segment of Formula 3.

In a sixth aspect, the invention is a method for reducing glare and/or reflectance on a substrate that includes coating the substrate with a composition with the polymer or polymeric material with the segment of Formula 3.

The details of one or more embodiments of the invention are set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and from the claims.

DETAILED DESCRIPTION

The invention is a naphthyloxyalkyl(meth)acrylate monomer with a high refractive index and whose respective homopolymer has a low glass transition temperature. The monomers have specific index of refraction, melting point, and viscosity properties that are particularly suited for use in polymeric materials intended for application to a substrate in an optical element or an optical device.

As used within the present description, "monomer" refers to a monomer on an individual (i.e., molecular) scale, and also to a composition of such monomers on a macroscopic scale such that the composition can be described as having a physical state of matter (e.g., liquid, solid, etc.) and physical properties (e.g., melting point, viscosity, glass transition temperature (of a polymeric form), and index of refraction).

The naphthyloxyalkyl(meth)acrylate monomers of the invention have an index of refraction of at least about 1.54, preferably between about 1.54 and 1.56. "Index of refraction," or "refractive index," refers to the absolute refractive index of a material (e.g., a monomer), which is understood to be the ratio of the speed of electromagnetic radiation in free space to the speed of the radiation in that material, with the radiation being of sodium yellow light at a wavelength of about 583.9 nanometers (nm). Index of refraction can be measured by known methods, and is generally measured using an Abbe Refractometer.

Homopolymers of the naphthyloxyalkyl(meth)acrylate monomers of the invention have a Tg below about 10 °C, preferably less than about 7 °C, and most preferably less than about 5 °C. "Glass transition temperature," (Tg), is the temperature range over which a thermoplastic polymer changes from a brittle, glass state to a plastic state. Glass transition temperature of a composition can be measured by methods known in the art, such as Differential Scanning Calorimetry (DSC), modulated DSC (MDSC), or Dynamic Mechanical Analysis (DMA).

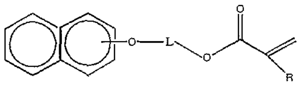
The naphthyloxyalkyl(meth)acrylate monomers include a (meth)acrylate functional group and a naphthyloxy functional group linked by an alkyl functional group.

The alkyl group is a divalent organic hydrocarbon group. The alkyl group, which is preferably unsubstituted, can be straight or branched and includes greater than 5 carbon atoms, more preferably from 6 to 8 carbon atoms. The size of the alkyl group can affect the physical properties of the monomer and a polymer prepared from the monomer including, for example, the refractive index of the monomer and the refractive index and glass transition temperature of a polymer prepared from the monomer. While not wishing to be bound by any theory, a relatively larger alkyl group may result in a monomer or a polymer with a relatively lower index of refraction compared to an otherwise similar monomer or polymer having a relatively smaller alkyl group. Again, while not wishing to be bound by any theory, relatively larger or more branched alkyl groups may provide a monomer which, when polymerized, has a relatively lower Tg compared to a polymer prepared from otherwise similar monomers having relatively smaller or less branched alkyl groups.

The naphthyloxy group in the monomer of the invention is also preferably unsubstituted.

The (meth)acrylate group in the monomer of the invention can be prepared by methods well known to those skilled in the art. The naphthyloxy alkanol intermediates can be esterified with (meth)acyloyl chloride using a suitable base. They can also be prepared by condensation with (meth)acrylic acid, or by transesterification using, for instance, methyl (meth)acylate. Suitable inhibitors can be added to the reactions during the synthesis of the monomers to prevent premature polymerization of the monomers.

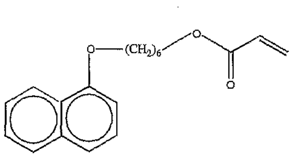
Examples of useful naphthyloxy alkyl acrylate monomers include those with the structure of Formula 2:



Formula 2

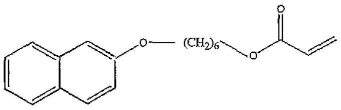
wherein L is a straight chain or branched alkyl group containing greater than 5 carbon atoms, preferably from about 6 to about 8 carbon atoms, and R is H or CH_3.

Examples of useful monomers include 6-(1-naphthyloxy)-1-hexylacrylate, wherein the oxyalkylacrylate group is located at the 1 or α position on the naphthalene ring structure and the alkyl unit has 6 carbon atoms. This monomer, shown below in Formula 4, has a refractive index of about 1.556 and the Tg of its homopolymer is about 3 °C.



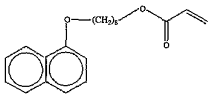
Formula 4

Another preferred monomer is 6-(2-naphthyloxy)-1-hexylacrylate, wherein the oxyalkylacrylate group is located at the 2 or β position on the naphthalene ring structure and the alkyl unit has 6 carbon atoms. This monomer, shown below in Formula 5, has a refractive index of about 1.553 and the Tg of its homopolymer is about 6 °C.



Formula 5

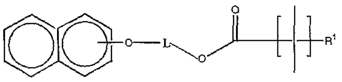
Another preferred monomer is 8-(1-naphthyloxy)-1-octylacrylate, wherein the oxyalkylacrylate group is located at the 1 or α position on the naphthalene ring structure and the alkyl unit has 8 carbon atoms. This monomer, shown below in Formula 6, has a refractive index of about 1.547 and the Tg of its homopolymer is about -49 °C.



Formula 6

The monomer of the invention, alone or in combination with materials such as other unsaturated polymerizable comonomers, can be included in a polymerizable composition that can be polymerized or co-polymerized to produce useful polymers or copolymers. As used within the present description, the term "polymerizable" refers to chemical compounds such as monomers and oligomers, etc., and chemical compositions, capable of polymerizing or copolymerizing (e.g., via unsaturated moieties) to produce a higher molecular weight materials such as an oligomer, polymer, prepolymer, or polymeric material. The terms "polymer" and "polymeric material" are used interchangeably to refer to materials prepared from the reaction of one or more polymerizable materials, e.g., one or more polymerizable monomer, oligomer, polymer, or prepolymer, etc., to produce a dimer, trimer, oligomer, copolymer, homopolymers, etc.

The polymers and polymeric materials include a chemical segment of Formula 3:



Formula 3

wherein L is a straight chain or branched alkyl group, preferably containing greater than 5 carbon atoms, preferably from about 6 to about 8 carbon atoms, and R^1 is H or CH_3.

Useful comonomers to be reacted with acrylic monomers such as the monomer described herein are known in the organic chemistry art, and can include any of a number of known and useful polymerizable moieties, e.g., vinyl, (meth)acrylate, N-vinyl, acrylic acid, methacrylic acid, allyl, acrylamide, acrylonitrile, etc. The comonomer can be mono- or multifunctional with respect to the unsaturated moiety, and where multifunctional, the unsaturated moieties need not be of identical chemistry.

Specific types of comonomers useful in the polymerizable composition can include (meth)acrylate-functional comonomers such as butyl (meth)acrylate, as well as vinyl comonomers such as methyl styrene. The particular comonomers included in any given polymerizable composition, their molecular weight or weights, and the included amounts of each, can be chosen according to various factors such as the desired nature and properties of the polymerizable composition and the desired properties of the polymer or polymeric material to be prepared therefrom (e.g., index of refraction, glass transition temperature, melting point, viscosity, etc., of the polymerizable composition or polymeric material).

The polymerizable composition can also contain other ingredients that, as will be appreciated by those skilled in the art of polymeric materials, can be useful in such a polymerizable composition. For example, the polymerizable composition might contain a crosslinking agent, one or more surfactants, pigments, fillers, polymerization inhibitors, or other ingredients that can be useful within a polymerizable composition or an optical product. Such ingredients can be included in the composition in amounts known to be effective for their respective purposes.

A crosslinking agent can be useful to increase the glass transition temperature of the polymer resulting from crosslinking the polymerizable composition.

Polymeric beads, inorganic fillers, and/or pigments can be added to the polymerizable composition in order to improve processing, to impart slip and scratch resistance to the polymerized material, or to affect optical properties of the polymerized material. Examples of useful polymeric beads include those made of polystyrene, polyacrylates, copolymers of styrene and acrylates, polyethylene, polypropylene, polytetrafluoroethylene, or combinations thereof. Examples of inorganic fillers and pigments include solid or hollow glass beads, silica, zirconia, aluminum trihydroxide, and titanium dioxide.

Polymerization of the polymerizable composition can be accomplished by known and usual means, such as heating in the presence of a free-radical initiator, irradiation with electromagnetic radiation such as ultraviolet or visible light in the presence of suitable photoinitiators, and by electron beam.

Polymeric materials (i.e., homopolymers or copolymers) prepared from the monomer of the invention have a Tg below about 10 °C, as well as a refractive index greater than about 1.54. This makes the polymers particularly well suited to use as coatings and adhesives on polymeric substrates used in optical elements and optical devices, such as, for example, polymethylmethacrylate (PMMA), polycarbonate (PC), and

continued for an additional hour after completing the addition. Gas chromatography (GC) analysis showed less than 1% residual starting material.

The reaction was cooled to room temperature. 366 g t-butyl methyl ether was added. The reaction mixture was stirred, then poured into a separatory funnel and allowed to phase split. The aqueous phase was removed and the organic phase washed with 6.9 g concentrated HCl in 125 g deionized water, then with 6.1 g NaCl in 125 g deionized water. The remaining solvent was stripped from the product using a rotary evaporator.

The product was distilled at a pot temperature of 220 - 260 °C and a head temperature of 200 - 230 °C at 0.1 - 0.2 mm Hg. This procedure yielded 63.5 g of a light brown, somewhat viscous liquid. GC showed it was at least 98% pure 6-(1-naphthyloxy)-1-hexanol.

A one-liter three-neck flask was equipped with a mechanical stirrer, temperature probe, and Dean-Stark trap with condenser was charged with the following reagents: 60 g 6-(1-naphthyloxy)-1-hexanol, 226 g toluene, 2.5 g para-toluene sulfonic acid, 21.2 g acrylic acid, 0.027 g hydroquinone, and 0.03 g 4-methoxyphenol. The mixture was heated to reflux, collecting the water, which evolved in the Dean-Stark trap. After three hours, thin layer chromatography showed the reaction was complete (i.e., no starting material remained).

The reaction was cooled to room temperature and 132 g deionized water was added. The mixture was put into a separatory funnel, shaken and allowed to phase split. The aqueous layer was removed and the organic phase was washed with 0.3 g concentrated HCl in 44 g deionized water, then with 1.3 g sodium carbonate in 44 g deionized water, and then with 1.4 g sodium chloride in 44 g deionized water. The remaining solvent was stripped using a rotary evaporator. The crude product residue was passed through a flash silica gel column eluting with a mixture of ethyl acetate/heptanes (5/95). The product fractions were collected and the solvent stripped using a rotary evaporator. The light greenish oil product crystallized on standing to give 45 g of off-white crystals with a melting point of 37 - 39 °C. GC and ^{13}C NMR analysis confirmed the product to be greater than 99% pure 6-(1-naphthyloxy)-1-hexyl acrylate (1-NOHA).

The refractive index of the 1-NOHA was 1.556 as measured using an Abbe Refractometer, made by Erma Inc. of Tokyo, Japan and distributed by Fisher Scientific.

Homopolymer was prepared by charging a 120 ml bottle with 2.0 g 1-NOHA monomer, 10 g ethyl acetate, and 0.06 g of a catalyst, available from E. I. DuPont De Nemours and Co., Wilmington, DE, under the trade designation VAZO 64. The bottle was deoxygenated by purging with nitrogen at a flow rate of 1 liter per minute for 35 seconds. The bottle was then sealed and placed in a rotating water bath at 55 °C for 24 hours to effect essentially complete polymerization. Polymer films were prepared by casting the polymer solution in an aluminum pan and evaporating the solvent in a 65 °C oven. Glass transition temperatures (Tg) were determined using a differential scanning calorimeter (DCS-7) manufactured by Perkin Elmer, Norwalk, CT. A 10 mg polymer sample was heated at a rate of 20 °C/minute, cooled at a rate of 40 °C/minute, and then reheated at 20 °C/minute. The Tg was calculated on the second heating cycle, and was calculated to be 6 °C.

Example 2

Synthesis of 8-(1-naphthyloxy)-1-octylacrylate (1-NOOA):

A 500 ml three-neck flask was equipped with a mechanical stirrer, temperature probe, and a condenser. The following reagents were added: 25 g 1-naphthol, 156 g deionized water, 2.6 g sodium iodide, and 27.7 g sodium hydroxide (50% in water). This mixture was heated to reflux. To the refluxing reaction was added 57.1 g 8-chloro-1-octanol dropwise through an addition funnel over a two-hour period. Heating at reflux was continued for one additional hour after completing the addition. GC showed less than 1% residual starting material.

The reaction was cooled to room temperature, and 207 g chloroform was added. The mixture was stirred, then poured into a separatory funnel, and allowed to phase split. The upper aqueous phase was separated out, and the organic phase was washed with 3.4 g concentrated HCl in 62 g deionized water, then with 3.0 g NaCl in 62 g deionized water. The solvent was stripped from the product using a rotary evaporator.

The product was then distilled, first removing residual 8-chloro-1-octanol at a head temperature of about 100 °C and 0.2 mm Hg. The product distilled at a head temperature of 180 - 200 °C at 0.1 mm Hg. About 17 g of 8-(1-naphthyloxy)-1-octanol was collected, which was a light orange color.

A 250 ml three-neck flask was equipped with a mechanical stirrer, temperature probe, and Dean-Stark trap with condenser. The following reagents were added: 14 g 8-(1-naphthyloxy)-1-octanol, 118 g toluene, 0.5 g para-toluene sulfonic acid, 4.5 g acrylic acid, 0.006 g hydroquinone, and 0.006 g 4-methoxyphenol. The mixture was heated to reflux, and the water that evolved was collected in the Dean-Stark trap. After three hours, thin layer chromatography showed that the reaction was complete.

The reaction was cooled to room temperature and 27 g deionized water was added. The mixture was shaken well in a separatory funnel, phase split, and the aqueous layer was removed. The organic phase was washed sequentially with 0.1 g concentrated HCl in 10 g deionized water, then with 0.3 g sodium carbonate in 10 g deionized water, then with 0.3 g sodium chloride in 10 g deionized water. The solvent was stripped using a rotary evaporator, and the crude product residue was passed through a flash silica gel column eluting with methylene chloride. The product fractions were collected and solvent stripped using a rotary evaporator, finishing by pulling on the flask with a vacuum pump to remove the last traces of solvent.

The light yellow oil product crystallized on standing to give 12 g of a wet semi-solid. GC and ^{13}C NMR confirmed that the product was greater than 99% pure 8-(1-naphthyloxy)-1-octylacrylate (1-NOOA).

The refractive index of the 1-NOOA was 1.547 as measured using an Abbe Refractometer, made by Erma Inc. of Tokyo, Japan and distributed by Fisher Scientific.

Homopolymer was prepared as described in Example 1 except 1-NOOA was used instead of 1-NOHA. The Tg of the homopolymer was -49 °C.

A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A naphthyloxyalkyl(meth)acrylate monomer with an index of refraction of greater than about 1.55 and whose respective homopolymer has a glass transition temperature of less than about 10 °C.

2. A naphthyloxyalkyl(meth)acrylate monomer comprising an alkyl functional group with at least 6 carbon atoms.

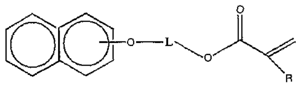
3. The monomer of claim 2, wherein the monomer has an index of refraction of greater than about 1.55 and whose respective homopolymer has a glass transition temperature of less than about 10 °C.

4. The monomer of claim 2, wherein the alkyl group has 6 carbon atoms.

5. The monomer of claim 2, wherein the alkyl group has 8 carbon atoms.

6. The monomer of claim 2, wherein the alkyl group is a straight chain.

7. The monomer of Formula 2, wherein L is a straight chain or branched alkyl group with greater than 5 carbon atoms and R is H or CH_3.



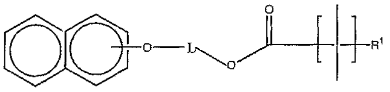
Formula 2

8. The monomer of claim 7, wherein L is a straight chain alkyl unit with 6 to 8 carbon atoms.

9. The monomer of claim 7, wherein L is a straight chain alkyl unit with 6 carbon atoms.

10. A polymerizable composition comprising the monomer of claim 7.

11. A polymer comprising a chemical segment of the Formula 3:



Formula 3

wherein L is a straight chain or branched alkyl group with greater than about 5 carbon atoms, and R^1 is H or CH_3.

12. An optical element comprising the polymer of claim 11.

13. An optical device comprising an optical element, wherein the optical element comprises the polymer of claim 11.

14. A method for reducing glare on a substrate comprising applying to the substrate the polymer of claim 11.

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(54) Title: NAPHTHYLOXYALKYL (METH) ACRYLATES WITH HIGH REFRACTIVE INDICES AND LOW GLASS TRANSITION TEMPERATURES

(57) Abstract: Naphthyloxyalkyl(meth)acrylate monomers having a high refractive index and whose respective homopolymer has a low glass transition temperature.

NAPHTHYLOXYALKYL(METH)ACRYLATES WITH HIGH REFRACTIVE INDICES AND LOW GLASS TRANSITION TEMPERATURES

TECHNICAL FIELD

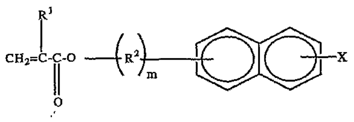
This invention relates to naphthyloxyalkyl(meth)acrylate compounds with a high refractive index and whose respective homopolymer has a low glass transition temperature.

BACKGROUND

Adhesives or coatings used in optical applications preferably have a refractive index closely matched to the refractive index of a substrate to which they are applied. The matched refractive indices reduce glare and reflectance at the interface between the substrate and coating materials and enhance the optical performance of the construction.

Polymeric substrate materials typically used in optical applications have refractive indices of about 1.48 to about 1.65, such as, for example, polymethyl(meth)acrylate (1.489), polycarbonate (1.585), and polyethylene terephthalate (1.64). However, many polymeric coatings and adhesives intended for application to these substrates have refractive indices that differ substantially from the refractive indices of the substrates. The mismatched refractive indices may cause glare and reflectance at the interface between the materials.

Reactive chemical monomers can be used, alone or in combination with other materials, to produce adhesives and coatings with high indices of refraction. However, these adhesive and coating compositions may have other less desirable physical and chemical properties. For example, certain naphthalene derivatives of Formula 1 below have an index of refraction of about 1.57 - 1.58:



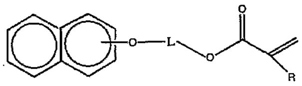
Formula 1

wherein R^1 is H or CH_3, R^2 is CH_2CH_2O or $CH(CH_3)CH_2O$, X is H, and m is 1. While the refractive index of the monomers in Formula 1 may match well with polymeric substrates commonly used in optical applications, homopolymers made from known compounds of this type typically have a glass transition temperature (Tg) of about 25 to about 40 °C. For this reason, polymers including these monomeric units would be expected to be essentially non-tacky at or near room temperature (about 20 to about 30 °C), which limits their usefulness in optical adhesives and flexible coatings.

SUMMARY

In one aspect, the invention is a naphthyloxyalkyl(meth)acrylate monomer with an index of refraction of greater than about 1.55 and a glass transition temperature of its respective homopolymer of less than about 10 °C. The naphthyloxyalkyl(meth)acrylate monomers include a (meth)acrylate functional group and a naphthyloxy functional group linked by an alkyl functional group.

The preferred naphthyloxyalkyl(meth)acrylate monomers of the invention have the general Formula 2:

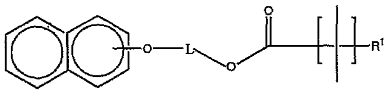


Formula 2

wherein L is a straight chain or branched alkyl group containing greater than 5 carbon atoms, preferably from about 6 to about 8 carbon atoms, and R is H or CH_3.

In a second aspect, the invention is a polymerizable composition containing the monomer of Formula 2. The polymerizable composition can contain one or more other compatible comonomers.

In a third aspect, the invention is a polymer or polymeric material including a chemical segment of Formula 3:



Formula 3

wherein L is a straight chain or branched alkyl group containing greater than 5 carbon atoms, preferably from about 6 to about 8 carbon atoms, and R^1 is H or CH_3. The polymers with the monomeric segment of Formula 3 have a low glass transition temperature of less than about 10 °C, and are well suited for use in optical adhesives and flexible coating compositions. The adhesives and coating compositions made from the monomers of the invention would be expected to reduce glare and reflectance when applied to a polymeric substrate with a similarly high refractive index.

In a fourth aspect, the invention is an optical element including a composition with the polymer or polymeric material with the segment of Formula 3.

In a fifth aspect, the invention is an optical device including a composition with the polymer or polymeric material with the segment of Formula 3.

In a sixth aspect, the invention is a method for reducing glare and/or reflectance on a substrate that includes coating the substrate with a composition with the polymer or polymeric material with the segment of Formula 3.

The details of one or more embodiments of the invention are set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and from the claims.

DETAILED DESCRIPTION

The invention is a naphthyloxyalkyl(meth)acrylate monomer with a high refractive index and whose respective homopolymer has a low glass transition temperature. The monomers have specific index of refraction, melting point, and viscosity properties that are particularly suited for use in polymeric materials intended for application to a substrate in an optical element or an optical device.

As used within the present description, "monomer" refers to a monomer on an individual (i.e., molecular) scale, and also to a composition of such monomers on a macroscopic scale such that the composition can be described as having a physical state of matter (e.g., liquid, solid, etc.) and physical properties (e.g., melting point, viscosity, glass transition temperature (of a polymeric form), and index of refraction).

The naphthyloxyalkyl(meth)acrylate monomers of the invention have an index of refraction of at least about 1.54, preferably between about 1.54 and 1.56. "Index of refraction," or "refractive index," refers to the absolute refractive index of a material (e.g., a monomer), which is understood to be the ratio of the speed of electromagnetic radiation in free space to the speed of the radiation in that material, with the radiation being of sodium yellow light at a wavelength of about 583.9 nanometers (nm). Index of refraction can be measured by known methods, and is generally measured using an Abbe Refractometer.

Homopolymers of the naphthyloxyalkyl(meth)acrylate monomers of the invention have a Tg below about 10 °C, preferably less than about 7 °C, and most preferably less than about 5 °C. "Glass transition temperature," (Tg), is the temperature range over which a thermoplastic polymer changes from a brittle, glass state to a plastic state. Glass transition temperature of a composition can be measured by methods known in the art, such as Differential Scanning Calorimetry (DSC), modulated DSC (MDSC), or Dynamic Mechanical Analysis (DMA).

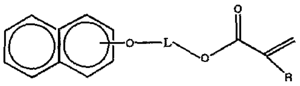
The naphthyloxyalkyl(meth)acrylate monomers include a (meth)acrylate functional group and a naphthyloxy functional group linked by an alkyl functional group.

The alkyl group is a divalent organic hydrocarbon group. The alkyl group, which is preferably unsubstituted, can be straight or branched and includes greater than 5 carbon atoms, more preferably from 6 to 8 carbon atoms. The size of the alkyl group can affect the physical properties of the monomer and a polymer prepared from the monomer including, for example, the refractive index of the monomer and the refractive index and glass transition temperature of a polymer prepared from the monomer. While not wishing to be bound by any theory, a relatively larger alkyl group may result in a monomer or a polymer with a relatively lower index of refraction compared to an otherwise similar monomer or polymer having a relatively smaller alkyl group. Again, while not wishing to be bound by any theory, relatively larger or more branched alkyl groups may provide a monomer which, when polymerized, has a relatively lower Tg compared to a polymer prepared from otherwise similar monomers having relatively smaller or less branched alkyl groups.

The naphthyloxy group in the monomer of the invention is also preferably unsubstituted.

The (meth)acrylate group in the monomer of the invention can be prepared by methods well known to those skilled in the art. The naphthyloxy alkanol intermediates can be esterified with (meth)acyloyl chloride using a suitable base. They can also be prepared by condensation with (meth)acrylic acid, or by transesterification using, for instance, methyl (meth)acylate. Suitable inhibitors can be added to the reactions during the synthesis of the monomers to prevent premature polymerization of the monomers.

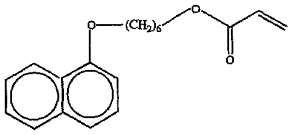
Examples of useful naphthyloxy alkyl acrylate monomers include those with the structure of Formula 2:



Formula 2

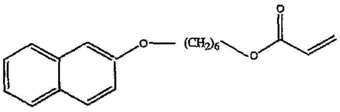
wherein L is a straight chain or branched alkyl group containing greater than 5 carbon atoms, preferably from about 6 to about 8 carbon atoms, and R is H or CH_3.

Examples of useful monomers include 6-(1-naphthyloxy)-1-hexylacrylate, wherein the oxyalkylacrylate group is located at the 1 or α position on the naphthalene ring structure and the alkyl unit has 6 carbon atoms. This monomer, shown below in Formula 4, has a refractive index of about 1.556 and the Tg of its homopolymer is about 3 °C.



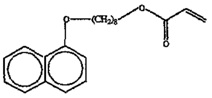
Formula 4

Another preferred monomer is 6-(2-naphthyloxy)-1-hexylacrylate, wherein the oxyalkylacrylate group is located at the 2 or β position on the naphthalene ring structure and the alkyl unit has 6 carbon atoms. This monomer, shown below in Formula 5, has a refractive index of about 1.553 and the Tg of its homopolymer is about 6 °C.



Formula 5

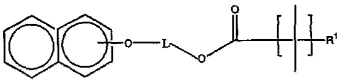
Another preferred monomer is 8-(1-naphthyloxy)-1-octylacrylate, wherein the oxyalkylacrylate group is located at the 1 or α position on the naphthalene ring structure and the alkyl unit has 8 carbon atoms. This monomer, shown below in Formula 6, has a refractive index of about 1.547 and the Tg of its homopolymer is about -49 °C.



Formula 6

The monomer of the invention, alone or in combination with materials such as other unsaturated polymerizable comonomers, can be included in a polymerizable composition that can be polymerized or co-polymerized to produce useful polymers or copolymers. As used within the present description, the term "polymerizable" refers to chemical compounds such as monomers and oligomers, etc., and chemical compositions, capable of polymerizing or copolymerizing (e.g., via unsaturated moieties) to produce a higher molecular weight materials such as an oligomer, polymer, prepolymer, or polymeric material. The terms "polymer" and "polymeric material" are used interchangeably to refer to materials prepared from the reaction of one or more polymerizable materials, e.g., one or more polymerizable monomer, oligomer, polymer, or prepolymer, etc., to produce a dimer, trimer, oligomer, copolymer, homopolymers, etc.

The polymers and polymeric materials include a chemical segment of Formula 3:



Formula 3

wherein L is a straight chain or branched alkyl group, preferably containing greater than 5 carbon atoms, preferably from about 6 to about 8 carbon atoms, and R^1 is H or CH_3.

Useful comonomers to be reacted with acrylic monomers such as the monomer described herein are known in the organic chemistry art, and can include any of a number of known and useful polymerizable moieties, e.g., vinyl, (meth)acrylate, N-vinyl, acrylic acid, methacrylic acid, allyl, acrylamide, acrylonitrile, etc. The comonomer can be mono- or multifunctional with respect to the unsaturated moiety, and where multifunctional, the unsaturated moieties need not be of identical chemistry.

Specific types of comonomers useful in the polymerizable composition can include (meth)acrylate-functional comonomers such as butyl (meth)acrylate, as well as vinyl comonomers such as methyl styrene. The particular comonomers included in any given polymerizable composition, their molecular weight or weights, and the included amounts of each, can be chosen according to various factors such as the desired nature and properties of the polymerizable composition and the desired properties of the polymer or polymeric material to be prepared therefrom (e.g., index of refraction, glass transition temperature, melting point, viscosity, etc., of the polymerizable composition or polymeric material).

The polymerizable composition can also contain other ingredients that, as will be appreciated by those skilled in the art of polymeric materials, can be useful in such a polymerizable composition. For example, the polymerizable composition might contain a crosslinking agent, one or more surfactants, pigments, fillers, polymerization inhibitors, or other ingredients that can be useful within a polymerizable composition or an optical product. Such ingredients can be included in the composition in amounts known to be effective for their respective purposes.

A crosslinking agent can be useful to increase the glass transition temperature of the polymer resulting from crosslinking the polymerizable composition.

Polymeric beads, inorganic fillers, and/or pigments can be added to the polymerizable composition in order to improve processing, to impart slip and scratch resistance to the polymerized material, or to affect optical properties of the polymerized material. Examples of useful polymeric beads include those made of polystyrene, polyacrylates, copolymers of styrene and acrylates, polyethylene, polypropylene, polytetrafluoroethylene, or combinations thereof. Examples of inorganic fillers and pigments include solid or hollow glass beads, silica, zirconia, aluminum trihydroxide, and titanium dioxide.

Polymerization of the polymerizable composition can be accomplished by known and usual means, such as heating in the presence of a free-radical initiator, irradiation with electromagnetic radiation such as ultraviolet or visible light in the presence of suitable photoinitiators, and by electron beam.

Polymeric materials (i.e., homopolymers or copolymers) prepared from the monomer of the invention have a Tg below about 10 °C, as well as a refractive index greater than about 1.54. This makes the polymers particularly well suited to use as coatings and adhesives on polymeric substrates used in optical elements and optical devices, such as, for example, polymethylmethacrylate (PMMA), polycarbonate (PC), and polyethyleneterephthalate (PET). For example, as described in copending U.S. Application No. 09/605,500, the polymers prepared from the monomers of the invention may be used to make pressure-sensitive adhesives to be applied to a substrate in an optical device. Polymers prepared from the monomers of the invention may also be used as a coating for an optical element in an optical device.

Compared to conventional polymers, the polymers made from the monomers of the invention have refractive indices that are more closely matched with the refractive indices of polymeric substrates commonly used in optical elements and devices. This refractive index match reduces glare and reflectance at any optical interface between the substrate and the polymers, so the polymers made from the monomers of the invention may be used as part of a method for reducing glare and/or reflectance on a substrate. The method includes coating the substrate with a composition with the polymer or polymeric material with the fragment of Formula 3.

The term “glare” as used herein means the average reflectance over a range of about 400 to about 700 nm. The term “reflectance” means the fraction of incident flux on a surface that is returned to into the same hemisphere whose base is the surface and which contains the incident radiation.

The invention will be more fully appreciated with reference to the following non-limiting examples in which the reaction components are given as grams (g) used or as weight percents (wt %), based on the total weight of the reaction mixtures which are nominally 100 wt %. Dimensions in English units are nominal and conversion to Metric units is approximate.

Example 1

Synthesis of 6-(1-naphthyloxy)-1-hexyl acrylate (1-NOHA):

A one-liter three-neck flask was equipped with a mechanical stirrer, temperature probe, and a condenser. The following reagents were added: 50 g 1-naphthol, 312 g deionized water, 5.2 g sodium iodide, and 55.4 g sodium hydroxide (50% in water). The mixture was heated to reflux. To the refluxing reaction 94.7 g 6-chloro-1-hexanol was added dropwise through an addition funnel over a two-hour period. Heating at reflux was continued for an additional hour after completing the addition. Gas chromatography (GC) analysis showed less than 1% residual starting material.

The reaction was cooled to room temperature. 366 g t-butyl methyl ether was added. The reaction mixture was stirred, then poured into a separatory funnel and allowed to phase split. The aqueous phase was removed and the organic phase washed with 6.9 g concentrated HCl in 125 g deionized water, then with 6.1 g NaCl in 125 g deionized water. The remaining solvent was stripped from the product using a rotary evaporator.

The product was distilled at a pot temperature of 220 - 260 °C and a head temperature of 200 - 230 °C at 0.1 - 0.2 mm Hg. This procedure yielded 63.5 g of a light brown, somewhat viscous liquid. GC showed it was at least 98% pure 6-(1-naphthyloxy)-1-hexanol.

A one-liter three-neck flask was equipped with a mechanical stirrer, temperature probe, and Dean-Stark trap with condenser was charged with the following reagents: 60 g 6-(1-naphthyloxy)-1-hexanol, 226 g toluene, 2.5 g para-toluene sulfonic acid, 21.2 g acrylic acid, 0.027 g hydroquinone, and 0.03 g 4-methoxyphenol. The mixture was heated to reflux, collecting the water, which evolved in the Dean-Stark trap. After three hours, thin layer chromatography showed the reaction was complete (i.e., no starting material remained).

The reaction was cooled to room temperature and 132 g deionized water was added. The mixture was put into a separatory funnel, shaken and allowed to phase split. The aqueous layer was removed and the organic phase was washed with 0.3 g concentrated HCl in 44 g deionized water, then with 1.3 g sodium carbonate in 44 g deionized water, and then with 1.4 g sodium chloride in 44 g deionized water. The remaining solvent was stripped using a rotary evaporator. The crude product residue was passed through a flash silica gel column eluting with a mixture of ethyl acetate/heptanes (5/95). The product fractions were collected and the solvent stripped using a rotary evaporator. The light greenish oil product crystallized on standing to give 45 g of off-white crystals with a melting point of 37 - 39 °C. GC and ^{13}C NMR analysis confirmed the product to be greater than 99% pure 6-(1-naphthyloxy)-1-hexyl acrylate (1-NOHA).

The refractive index of the 1-NOHA was 1.556 as measured using an Abbe Refractometer, made by Erma Inc. of Tokyo, Japan and distributed by Fisher Scientific.

Homopolymer was prepared by charging a 120 ml bottle with 2.0 g 1-NOHA monomer, 10 g ethyl acetate, and 0.06 g of a catalyst, available from E. I. DuPont De Nemours and Co., Wilmington, DE, under the trade designation VAZO 64. The bottle was deoxygenated by purging with nitrogen at a flow rate of 1 liter per minute for 35 seconds. The bottle was then sealed and placed in a rotating water bath at 55 °C for 24 hours to effect essentially complete polymerization. Polymer films were prepared by casting the polymer solution in an aluminum pan and evaporating the solvent in a 65 °C oven. Glass transition temperatures (Tg) were determined using a differential scanning calorimeter (DCS-7) manufactured by Perkin Elmer, Norwalk, CT. A 10 mg polymer sample was heated at a rate of 20 °C/minute, cooled at a rate of 40 °C/minute, and then reheated at 20 °C/minute. The Tg was calculated on the second heating cycle, and was calculated to be 6 °C.

Example 2

Synthesis of 8-(1-naphthyloxy)-1-octylacrylate (1-NOOA):

A 500 ml three-neck flask was equipped with a mechanical stirrer, temperature probe, and a condenser. The following reagents were added: 25 g 1-naphthol, 156 g deionized water, 2.6 g sodium iodide, and 27.7 g sodium hydroxide (50% in water). This mixture was heated to reflux. To the refluxing reaction was added 57.1 g 8-chloro-1-octanol dropwise through an addition funnel over a two-hour period. Heating at reflux was continued for one additional hour after completing the addition. GC showed less than 1% residual starting material.

The reaction was cooled to room temperature, and 207 g chloroform was added. The mixture was stirred, then poured into a separatory funnel, and allowed to phase split. The upper aqueous phase was separated out, and the organic phase was washed with 3.4 g concentrated HCl in 62 g deionized water, then with 3.0 g NaCl in 62 g deionized water. The solvent was stripped from the product using a rotary evaporator.

The product was then distilled, first removing residual 8-chloro-1-octanol at a head temperature of about 100 °C and 0.2 mm Hg. The product distilled at a head temperature of 180 - 200 °C at 0.1 mm Hg. About 17 g of 8-(1-naphthyloxy)-1-octanol was collected, which was a light orange color.

A 250 ml three-neck flask was equipped with a mechanical stirrer, temperature probe, and Dean-Stark trap with condenser. The following reagents were added: 14 g 8-(1-naphthyloxy)-1-octanol, 118 g toluene, 0.5 g para-toluene sulfonic acid, 4.5 g acrylic acid, 0.006 g hydroquinone, and 0.006 g 4-methoxyphenol. The mixture was heated to reflux, and the water that evolved was collected in the Dean-Stark trap. After three hours, thin layer chromatography showed that the reaction was complete.

The reaction was cooled to room temperature and 27 g deionized water was added. The mixture was shaken well in a separatory funnel, phase split, and the aqueous layer was removed. The organic phase was washed sequentially with 0.1 g concentrated HCl in 10 g deionized water, then with 0.3 g sodium carbonate in 10 g deionized water, then with 0.3 g sodium chloride in 10 g deionized water. The solvent was stripped using a rotary evaporator, and the crude product residue was passed through a flash silica gel column eluting with methylene chloride. The product fractions were collected and solvent stripped using a rotary evaporator, finishing by pulling on the flask with a vacuum pump to remove the last traces of solvent.

The light yellow oil product crystallized on standing to give 12 g of a wet semi-solid. GC and ^{13}C NMR confirmed that the product was greater than 99% pure 8-(1-naphthyloxy)-1-octylacrylate (1-NOOA).

The refractive index of the 1-NOOA was 1.547 as measured using an Abbe Refractometer, made by Erma Inc. of Tokyo, Japan and distributed by Fisher Scientific.

Homopolymer was prepared as described in Example 1 except 1-NOOA was used instead of 1-NOHA. The Tg of the homopolymer was -49 °C.

A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A naphthyloxyalkyl(meth)acrylate monomer with an index of refraction of greater than about 1.55 and whose respective homopolymer has a glass transition temperature of less than about 10 °C.

2. A naphthyloxyalkyl(meth)acrylate monomer comprising an alkyl functional group with at least 6 carbon atoms.

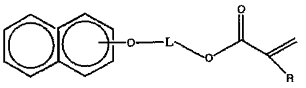
3. The monomer of claim 2, wherein the monomer has an index of refraction of greater than about 1.55 and whose respective homopolymer has a glass transition temperature of less than about 10 °C.

4. The monomer of claim 2, wherein the alkyl group has 6 carbon atoms.

5. The monomer of claim 2, wherein the alkyl group has 8 carbon atoms.

6. The monomer of claim 2, wherein the alkyl group is a straight chain.

7. The monomer of Formula 2, wherein L is a straight chain or branched alkyl group with greater than 5 carbon atoms and R is H or CH_3.



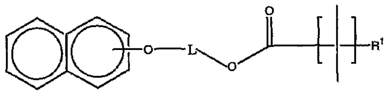
Formula 2

8. The monomer of claim 7, wherein L is a straight chain alkyl unit with 6 to 8 carbon atoms.

9. The monomer of claim 7, wherein L is a straight chain alkyl unit with 6 carbon atoms.

10. A polymerizable composition comprising the monomer of claim 7.

11. A polymer comprising a chemical segment of the Formula 3:



Formula 3

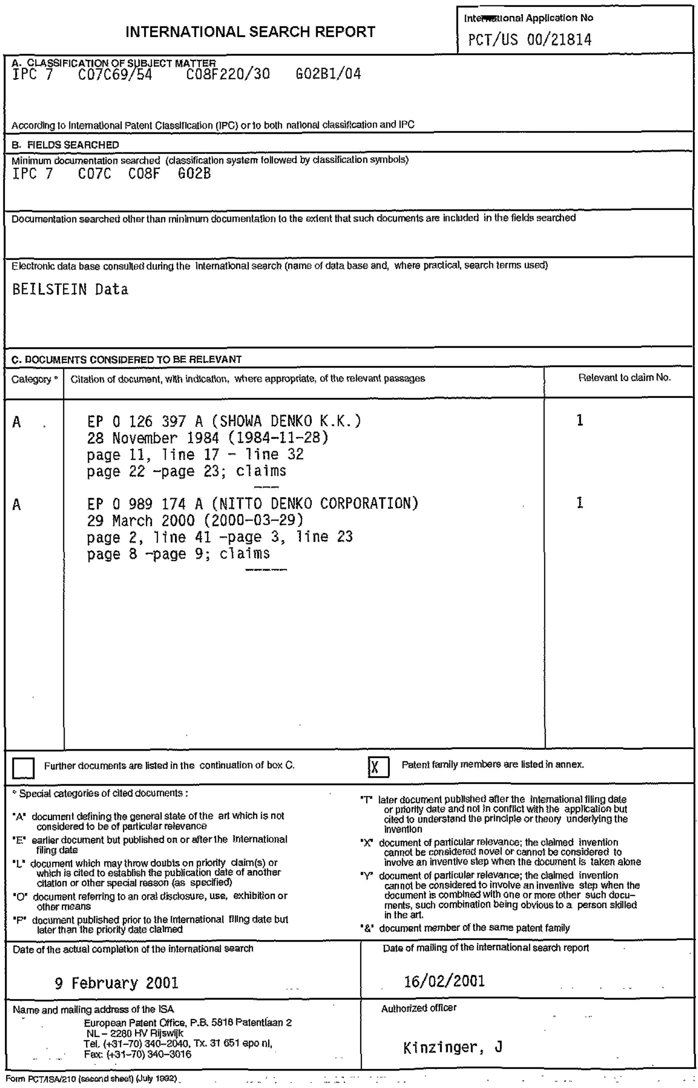
wherein L is a straight chain or branched alkyl group with greater than about 5 carbon atoms, and R^1 is H or CH_3.

12. An optical element comprising the polymer of claim 11.

13. An optical device comprising an optical element, wherein the optical element comprises the polymer of claim 11.

14. A method for reducing glare on a substrate comprising applying to the substrate the polymer of claim 11.

【国際調査報告】



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/21814

A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 126 397 A (SHOWA DENKO K.K.) 28 November 1984 (1984-11-28) page 11, line 17 - line 32 page 22 -page 23; claims	1
A	EP 0 989 174 A (NITTO DENKO CORPORATION) 29 March 2000 (2000-03-29) page 2, line 41 -page 3, line 23 page 8 -page 9; claims	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 9 February 2001	Date of mailing of the international search report 16/02/2001
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte[illegible]ional Application No
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